PADAMOT

Palaeohydrogeological Data Analysis and Model Testing

Fifth Framework Programme

PADAMOT: Project Overview Report

PADAMOT Project – EU FP5 Contract No FIKW-CT2001-20129

Technical Report

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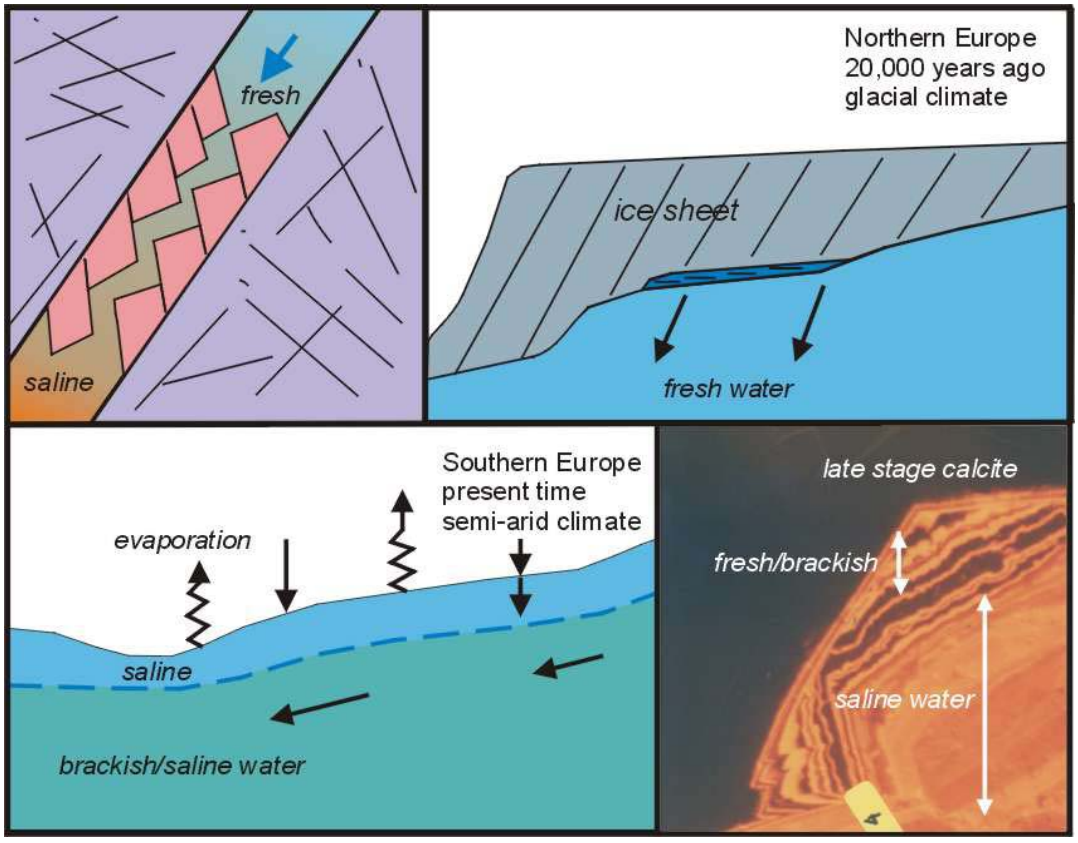

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PADAMOT PROJECT
TECHNICAL REPORT

PADAMOT: Project Overview Report

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Foreword

PADAMOT, 'Palaeohydrogeological Data Analysis and Model Testing', is a project within the European Union's 5th Framework RTD programme in nuclear fission safety (Contract Number FIKW-CT-2001-00129). It aims to improve the understanding of past groundwater conditions that supports assessments of future long-term safety of repositories for radioactive wastes. The project began in December 2001 with a duration of 36 months. The consortium of organisations involved in the PADAMOT project comprises:

United Kingdom Nirex Limited (UK)

Svensk Kärnbränslehantering AB (Sweden)

Terralogica AB (Sweden)

Empresa Nacional de Residuos Radioactivos S.A. (Spain)

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (Spain)

Intellisci Ltd (UK)

British Geological Survey (UK)

Charles University (Czech Republic)

University of Edinburgh (UK)

Universidad Politecnica de Madrid - School of Mines (Spain)

Safety assessments of proposed repositories for the long-term storage or disposal of radioactive wastes must take into account scenarios for environmental change over the long period of time during which the waste will be a hazard, typically up to one million years into the future. The scientific consensus in a number of countries is that disposing of long-lived and/or higher activity radioactive wastes and spent nuclear fuel deep underground in a 'geological repository' is the preferred option for long-term radioactive waste management. The reasons for preferring this option are that the host rock for a deep repository should provide stable conditions for performance of the engineered barrier system and that the rock mass separating a repository from the surface environment is a further barrier to radionuclide migration.

During the last two million years (the Quaternary Period), global climate has fluctuated between extremes of ice ages and warmer conditions than at present. Over various intervals in the past, large areas of northern Europe were covered by ice sheets and experienced extensive permafrost, whilst southern Europe was sometimes more pluvial (wetter). Consequently, the present-day climate is not representative of the climate that has existed for much of the Quaternary. This natural pattern of climatic fluctuation is expected to continue into the future, albeit modified by the impacts of anthropogenic greenhouse gas emissions. Variations in climate and in other environmental factors may affect future movements and compositions of groundwaters in the vicinity of a repository and thus affect the mobility of radionuclides and the rate of their migration back to the surface. It could be argued, therefore, that present-day groundwater conditions may not be an adequate basis for assessing long-term repository safety. However, if it can be demonstrated that, despite significant environmental change at the surface, groundwater flows and compositions at depth remain stable or change in a way that does not impact significantly on safety, then confidence in repository concepts for disposal will be increased.

PADAMOT has sought to address the following questions. How can such groundwater stability be assessed, with respect to climate-driven environmental change? In particular, what evidence is there that a deep geological repository will eliminate or reduce the effects of extreme changes in environmental conditions in the long term? In seeking to answer these questions, PADAMOT

has investigated geosphere systems at various European sites, using analytical methods and numerical modelling.

PADAMOT has comprised five work packages (WPs) with the following tasks:

WP1. Convening a preliminary workshop of PA specialists, PADAMOT researchers and other geoscientists on the use of palaeohydrogeology in PA.

WP2. Making palaeohydrogeological data measurements on mineral samples and groundwaters from sites in Spain, Czech Republic, Sweden and UK, using high resolution and high precision analytical methods, e.g. ion probe and laser ablation.

WP3. Constructing a relational database and a public domain website to store data from EQUIP and PADAMOT, accessible to project partners and to external researchers via the internet.

WP4. Developing numerical models to test palaeohydrogeological information interpreted from proxy geochemical, mineralogical and isotopic data, based on understanding of the processes that link the proxy data with climate-driven groundwater phenomena.

WP5. Synthesising project outcomes and disseminating an improved approach to the use of palaeohydrogeological information in the description of FEPs and hydrogeological scenarios for PA.

There are final reports from each of the five WPs plus this Overview report[1]:

Technical Report WP1.	The Long-Term Stability of Groundwater Conditions at Repository Sites: Proceedings of the PADAMOT Workshop, Brussels 2002.
Technical Report WP2.	Application of Mineralogical, Petrological and Geochemical Tools for Evaluating the Palaeohydrogeological Evolution of the PADAMOT Study Sites.
Technical Report WP3.	Design and Compilation of Database: Final Report.
Technical Report WP4.	Interpretative Modelling of Palaeohydrogeological Data: Final Report.
Technical Report WP5.	Dissemination and Use of Palaeohydrogeological Results for Safety Assessment.
Summary Report.	PADAMOT: Project Overview Report.

Further Information

Further information on the PADAMOT programme can be obtained from the project website http://www.bgs.ac.uk/padamot

[1] Copies of reports are available on request from the Project Co-ordinator: Paul Degnan (paul.degnan@nirex.co.uk)

Executive Summary

Background and relevance to radioactive waste management

International consensus confirms that placing radioactive wastes and spent nuclear fuel deep underground in a geological repository is the generally preferred option for their long-term management and disposal. This strategy provides a number of advantages compared to leaving it on or near the Earth's surface. These advantages come about because, for a well chosen site, the geosphere can provide:

- a physical barrier that can negate or buffer against the effects of surface dominated natural disruptive processes such as deep weathering, glaciation, river and marine erosion or flooding, asteroid/comet impact and earthquake shaking etc.
- long and slow groundwater return pathways from the facility to the biosphere along which retardation, dilution and dispersion processes may operate to reduce radionuclide concentration in the groundwater.
- a stable, and benign geochemical environment to maximise the longevity of the engineered barriers such as the waste containers and backfill in the facility.
- a natural radiation shield around the wastes.
- a mechanically stable environment in which the facility can be constructed and will afterwards be protected.
- an environment which reduces the likelihood of the repository being disturbed by inadvertent human intrusion such as land use changes, construction projects, drilling, quarrying and mining etc.
- protection against the effects of deliberate human activities such as vandalism, terrorism and war etc.

However, safety considerations for storing and disposing of long-lived radioactive wastes must take into account various scenarios that might affect the ability of the geosphere to provide the functionality listed above. Therefore, in order to provide confidence in the ability of a repository to perform within the deep geological setting at a particular site, a demonstration of geosphere "stability" needs to be made. Stability is defined here to be the capacity of a geological and hydrogeological system to minimise the impact of external influences on the repository environment, or at least to account for them in a manner that would allow their impacts to be evaluated and accounted for in any safety assessments.

A repository should be sited where the deep geosphere is a stable host in which the engineered containment can continue to perform according to design and in which the surrounding hydrogeological, geomechanical and geochemical environment will continue to operate as a natural barrier to radionuclide movement towards the biosphere. However, over the long periods of time during which long-lived radioactive wastes will pose a hazard, environmental change at the surface has the potential to disrupt the stability of the geosphere and therefore the causes of environmental change and their potential consequences need to be evaluated.

As noted above, environmental change can include processes such as deep weathering, glaciation, river and marine erosion. It can also lead to changes in groundwater boundary conditions through alternating recharge/discharge relationships. One of the key drivers for environmental change is climate variability. The question then arises, how can geosphere

stability be assessed with respect to changes in climate? Key issues raised in connection with this are:

- What evidence is there that 'going underground' eliminates the extreme conditions that storage on the surface would be subjected to in the long term?
- How can the additional stability and safety of the deep geosphere be demonstrated with evidence from the natural system?

As a corollary to this, the capacity of repository sites deep underground in stable rock masses to mitigate potential impacts of future climate change on groundwater conditions therefore needs to be tested and demonstrated. To date, generic scenarios for groundwater evolution relating to climate change are currently weakly constrained by data and process understanding. Hence, the possibility of site-specific changes of groundwater conditions in the future can only be assessed and demonstrated by studying groundwater evolution in the past. Stability of groundwater conditions in the past is an indication of future stability, though both the climatic and geological contexts must be taken into account in making such an assertion.

Palaeohydrogeology and investigation of groundwater stability

PADAMOT has addressed these questions and issues through palaeohydrogeology, i.e. by looking at evidence for groundwater conditions in the past that is recorded in the rock mass and present-day groundwater system. In particular, the project has investigated how minerals and groundwater at a number of sites have evolved and has interpreted how minerals have recorded past changes in groundwater conditions. The integration of information has led to inferences about how those changes might be related to past climate changes and then leads to some conclusions about the degree to which climate changes have affected groundwater conditions at various depths.

During the Quaternary period, i.e. the last two million years or so, global climate has alternated between cold climate states, characterised by extensive permafrost/ice sheets/glaciers, and climate states warmer than the present. In northerly latitudes, the potential for cold region processes to affect groundwater pathways, fluxes, residence times and hydrochemistry is significant, whilst for southern European localities the alternation between pluvial and arid conditions is equally important as a potential control on groundwater conditions. Consequently, the present-day climate is not representative of the climate that has existed for much of the Quaternary. This natural pattern of climatic fluctuation is expected to continue into the future, albeit modified by the impacts of anthropogenic greenhouse gas emissions.

Project objectives and partners

PADAMOT has built on the outcomes of the European Union funded FP4 ‘PALHY’ cluster of projects: EQUIP ('Evidence from Quaternary Infills for Palaeohydrogeology'; Bath et al., 2000a), PHYMOL (‘A Palaeohydrogeological Study of the Mol Site’; Marivoet et al., 2000) and PAGEPA (‘Palaeohydrogeology and Geoforecasting for Performance Assessment in Geosphere Repositories for Radioactive Waste Disposal’; Boulton et al., 2001). These developed palaeohydrogeological methods and improved our understanding of change and stability in groundwater systems in relevant geosphere settings over timescales in the past that mirror the future timescales of repository safety assessments. The main activities in PADAMOT have been (i) the analysis and interpretation of ‘proxies’ that indicate various aspects of groundwater conditions in the past, and (ii) the development of models that use data from the proxy indicators to produce palaeohydrogeological and geochemical information about past changes and stability that constrains scenarios for future evolution of geospheres at the study sites.

The project team has comprised partners from ten organisations in the European Union: radioactive waste management agencies, consultancies, research organisation and universities. The partners were: United Kingdom Nirex Limited (UK), SKB (Sweden), ENRESA (Spain), Terralogica AB (Sweden), CIEMAT (Spain), Universidad Politecnica de Madrid (Spain), Charles University Prague (Czech Republic), University of Edinburgh (UK), Intellisci (UK) and the British Geological Survey (UK). Additional support has been provided by the national radioactive waste management agency RAWRA (Czech Republic) and specialised research was carried out on behalf of ENRESA by Universidad de la Coruña (Spain). The project was co-ordinated by Nirex.

Project structure and work packages

The work was managed and carried out in five work packages (WPs) as follows:

WP1 comprised a workshop to discuss and document how the existing state of expertise and knowledge in palaeohydrogeology could be taken forward in PADAMOT. Two tracks of enquiry were addressed: (i) identifying how palaeohydrogeological methods, data and uncertainties relate to the concept of groundwater stability, and (ii) how the knowledge gained from these studies could be used effectively in future performance assessments.

Workshop participants included safety assessment experts, site characterisation personnel and geoscientists investigating aspects of groundwater stability with palaeohydrogeological methods and using the results in site interpretations and safety cases. The workshop presented up-to-date views of investigation techniques, the types and accuracy of data that can be obtained, the uncertainties in these data, and the methods for integrated interpretations that can be effectively used in performance assessment (PA). A key part of the workshop was the involvement of independent expert facilitators to synthesise issues. The outcomes from the workshop endorsed the need for data to support the development of conceptual and numerical models and for information to improve the selection and descriptions of FEPs ('features, events and processes') that define scenarios in PA. The Proceedings of the workshop have been published as the WP1 Technical Report.

In WP2, mineralogical and geochemical measurements were made on late-stage fracture mineral and water samples from groundwater systems in Spain, Sweden, the UK and the Czech Republic with the aim of detecting and interpreting indicators of the recent palaeohydrogeological evolution of the groundwater systems. The palaeohydrogeology of the sites at Äspö/Laxemar in southeast Sweden and Sellafield in northwest England were previously studied during the earlier FP4 EQUIP project. Two Quaternary sedimentary sequences at Cúllar-Baza and Padul in south-eastern Spain had also been studied in EQUIP to provide a number of proxies for reconstruction of the regional palaeoclimatic history. These sites were examined further during PADAMOT to obtain new data to further evaluate and understand the palaeohydrogeological history of the sites. In addition, materials were studied from new sites at Dounreay and Cloud Hill (United Kingdom), Los Ratones (Spain), Laxemar (Sweden) and the Melechov Massif (Czech Republic).

The principal objectives were to obtain a broader generic understanding of the palaeohydrogeological information that can be recorded by fracture minerals, and to test the applicability of relationships between mineralogical features and palaeohydrogeology to other sites. Analytical methods were improved over previous studies and new methods applied (e.g. ion microprobe, laser ablation mass spectrometry, biomarker analysis) to obtain mineral, trace element and isotopic data at a finer (spatial and temporal) resolution. This achieved many improvements in the palaeohydrogeological interpretations. This work is reported in full in the WP2 Technical Report.

In WP3, a relational database was constructed to store pre-existing data from the EQUIP project and new data from PADAMOT. The database was designed to store all the data acquired in a consistent manner that was readily accessible to all the contributing partners via the internet. A

PADAMOT website was also implemented and this can be viewed at http://www.bgs.ac.uk/padamot. It contains useful information on the project and on palaeohydrogeology in general and is a gateway to the database. The database and website will be maintained beyond the project lifetime and external researchers will have free access to the database on request. A comprehensive report on the database design is provided as the WP3 Technical Report.

In WP4, numerical interpretative models were developed and demonstrated to test and improve our understanding of palaeohydrogeological information obtained from geochemical and mineralogical 'proxy' data. The potential value of palaeohydrogeology in Performance Assessment (PA) is in understanding better the time-varying changes of the groundwater flux and flow direction, chemical environment, and other scenarios that are related to climate or other external environmental changes. Proxy data are interpreted using expert judgement and quantitative modelling to extract information that is relevant to PA. Interpretative models have been developed with particular focus on the processes that are relevant to data that has been acquired in WP2 from the sites in Spain (Los Ratones), UK (Sellafield) and Czech Republic (Melechov). Essentially, the interpretative models for process-understanding can be calibrated using palaeohydrological information and thus provide interfaces between palaeohydrogeological information and FEPs (features, events and processes) for scenario development in PA.

For Los Ratones, the objective was to investigate the ways that climate changes might be propagated into groundwater recharge and thence into changes in groundwater compositions and ultimately into the geochemical and mineralogical proxies. This involved the integration of models for surface water mass balance, groundwater flow and reactive transport of solutes. For Sellafield, the objective has been to simulate the geochemical reactions that might have accounted for precipitation of late-stage calcites in fractured rock groundwater systems and to understand the significance of variations of Fe and Mn contents of secondary calcite with respect to past redox conditions in groundwater systems. Equilibrium modelling has been carried out for a range of batch mixing and reaction conditions and this has been supplemented by some coupled transport and reaction modelling. For Melechov, the objective was to understand groundwater conditions in the western part of the granite massif, using the results of a hydrogeological survey with numerical modelling of the spatial distribution of hydraulic potential, groundwater flows and travel times. This is the initial stage in the development of a site investigation methodology that is appropriate for fractured granitic rocks in the terrain and climate of the Bohemian massif. Modelling in WP4 has made progress towards the integration of models of biosphere/climate, groundwater and geochemistry for improving the use of palaeohydrogeology in PA. The modelling methods and results are provided in full in the WP4 Technical Report.

In WP5, existing safety cases were reviewed to find out the extent to which palaeohydrogeological data were considered and translated into information that could be used in PA. To improve this translation, it is proposed that interpretation of palaeohydrogeology should focus on input to the screening of Features, Events and Processes (FEPs) in the PA process. FEPs provide a context for palaeohydrogeological information that is recognised in PA. The uncertainties that are inherent in proxy data for palaeohydrogeology and in the interpretative models were assessed because an understanding of these issues is necessary for confidence in the proposed uses of data. The results from PADAMOT studies in WP2 and WP4 were synthesised and evaluated in terms of screening of FEPs and of more general insights of change or stability in groundwater conditions and thus of more realistic scenarios. Logical procedures for using palaeohydrogeological data more consistently and effectively are described in detail in the WP5 Technical Report, illustrating the steps of data acquisition, interpretation and expert judgement that should be used to quantify information for transfer into FEPs and scenarios.

Investigated sites

Fracture-flow groundwater systems at six European sites were studied:

- Melechov Hill, in the Bohemian Massif of the Czech Republic: a shallow (0-100 m) dilute groundwater flow system within the near-surface weathering zone in fractured granitic rocks;
- Cloud Hill, in the English Midlands: a (~100 m) shallow dilute groundwater flow system in fractured and dolomitized Carboniferous limestone;
- Los Ratones, in southwest Spain: an intermediate depth (0-500 m) dilute groundwater flow system in fractured granitic rocks;
- Laxemar, in southeast Sweden: a deep (0-1000 m) groundwater flow system in fractured granitic rocks. This is a complex groundwater system with potential recharge and flushing by glacial, marine, lacustrine and freshwater during the Quaternary;
- Sellafield, in northwest England: a deep (0-2000 m) groundwater flow system in fractured Ordovician low-grade metamorphosed volcaniclastic rocks and discontinuous Carboniferous Limestone, overlain by a Permo-Triassic sedimentary sequence with fracture and matrix porosity. This is a complex coastal groundwater system with deep hypersaline sedimentary basinal brines, and deep saline groundwaters in crystalline basement rocks, overlain by a shallow freshwater aquifer system. The site was glaciated several times during the Quaternary and may have been affected by recharge from glacial meltwater;
- Dounreay, in northeast Scotland: a deep (0-1400 m) groundwater flow system in fractured Precambrian crystalline basement overlain by fractured Devonian sedimentary rocks. This is within the coastal discharge area of a complex groundwater system, comprising deep saline groundwater hosted in crystalline basement, overlain by a fracture-controlled freshwater sedimentary aquifer system. Like Sellafield, this area experienced glaciation and may potentially record the impact of glacial meltwater recharge.

In addition, a study has been made of two Quaternary sedimentary sequences in Andalusia in south-eastern Spain to provide a basis for estimating the palaeoclimatic history of the region that can be used in any reconstruction of the palaeoclimatic history at the Los Ratones site:

- A lacustrine sedimentary sequence in the Cúllar-Baza basin records information about precipitation and palaeotemperature regimes, derived largely from the analysis of the stable isotope ($\delta^{18}O$ and $\delta^{13}C$) signatures from biogenic calcite (ostracod shells).
- A peat deposit at Padul provided information on past vegetation cover and palaeogroundwater inputs based on the study of fossil pollen and biomarkers as proxies for past climate change.

Results from analytical mineralogy and geochemistry

As a result of PADAMOT, calcite morphology has now been studied at several sites (Sellafield, Dounreay, Äspö, Laxemar and Cloud Hill). At Sellafield, Dounreay and Cloud Hill, it has been shown that there is a relationship between the crystal morphology of late-stage calcite mineralization and either present or past groundwater compositions, as demonstrated by fluid inclusion studies. This confirms observations from previous studies at Sellafield (Milodowski et al., 1997, 1998a, 2002), which demonstrated that the crystal morphology of the late-stage calcite mineralization varied systematically with groundwater salinity. Limited studies at Äspö during the EQUIP project also indicated that there was a relationship between calcite morphology and groundwater salinity. However, this relationship is not so clear at the Laxemar site, although here the variations in calcite morphology can be interpreted in terms of palaeo-variations in salinity, principally because of fluid inclusion evidence and by analogy with Sellafield. However, the relationship with present groundwater chemistry is unclear. It was also found that

the occurrence and distribution of late calcite in fractures in drill cores can be used to identify and predict the location of potential flowing features in the boreholes at all of these sites.

Calcite precipitated in freshwater characteristically forms short *c*-axis crystals, whereas in saline groundwaters the calcite morphology is characterized by *c*-axis elongated crystal forms. Examination of calcite growth zoning using cathodoluminescence or microchemical mapping provides a means of following the morphological changes during the growth of the calcite, thereby proving a proxy for the evolution of the salinity of the groundwater system. Calcite morphology therefore provides a sensitive indicator of changes in palaeosalinity in dilute groundwater systems, and can be used to differentiate fresh from brackish or saline groundwaters. In this respect, it has potential advantages over the use of fluid inclusion studies where this salinity differentiation is severely limited. However, the change from brackish to very saline groundwaters or brines is not marked by any obvious morphological change. Fluid inclusions studies provide a better means of monitoring changes within this higher salinity range.

Los Ratones

It is considered that, apart from the anthropogenic changes due to the mine itself, the greatest possibility of discontinuous change in the groundwater system would be fluctuations of the water table and hydraulic gradient synchronously with arid-pluvial cycles of climate. Site investigations have concluded that mineralogy is not a substantial source of evidence for hydrodynamic changes and provides only scant evidence for geochemical changes. Most of the groundwater system that has been investigated so far comprises a slowly weathering geochemical environment, dissolving calcite and not precipitating it. Therefore calcite, which was the main focus of secondary mineral studies in PADAMOT, is not a viable source of palaeohydrogeological information here. The extent to which groundwater conditions have fluctuated over time is not evident from this or other types of geochemical data. Data from chemical and isotopic analyses of groundwaters, carried out outside this project, are also not explicitly diagnostic of palaeohydrogeology although they assist in identifying the structural controls on flowpaths and hydrochemical mixing in pre- and post-mining groundwater regimes at Ratones (Gómez et al., 1999; Gómez, 2002).

Overall, it can be concluded that the mineralogical and geochemical methods promoted by PADAMOT have not been useful in furthering our understanding of the shallow weathering regime at Los Ratones, except in so far as new techniques have been tried and tested and the experience will allow decisions to be more confidently made in the future when assessing research options. The palaeohydrogeological research undertaken in PADAMOT has not been able to provide significant support to the successful development of integrated theory-based time-dependent modelling of the groundwater system. However the methods might be useful in any future testing below presently-investigated depths at this type of site to investigate how deeply oxidising and dissolving geochemical conditions have penetrated at different times.

Laxemar/Äspö

Mineralogical and isotopic properties of secondary calcites are distinct in the brackish-marine and meteoric-glacial groundwater regimes at intermediate depths and deep locations respectively in the Äspö and Laxemar systems. The resulting information about past distributions of groundwater masses supplements the palaeohydrogeological interpretation of sampled groundwater compositions by qualitatively indicating the sensitivity of these distributions to temporal changes of boundary conditions (Tullborg, 2004; SKB, 2004). This provides valuable input to scenario development, but its qualitative nature limits its value for testing the validity of palaeohydrogeological modelling. Data are primarily limited by the sampling limitations and challenges imposed by sparse secondary minerals. Two cautionary comments on the PADAMOT methodology are that interpretative models for morphology variations are presently generic and rely on calibrations of morphology versus salinity in Sellafield calcites, and that secondary minerals provide a discontinuous record which omits periods of mineral dissolution. It has been observed that late-stage secondary calcites are localised in certain fracture zones,

with different calcite generations distinguished by their morphologies. This is significant for PA in showing the persistence over time of the spatial distribution of water flow paths.

Overall, the PADAMOT methodology for palaeohydrogeology provides some important indications of the breadth of variability that PA scenarios should consider for the Laxemar/Äspö groundwater systems. As in the Sellafield case, a quantitative output to interpretative models is however, not possible.

Sellafield, Dounreay and Cloud Hill

Additional petrographic analyses of late stage calcite in drillcore samples from past site investigations at Sellafield in northwest England have consolidated the findings from previous work carried out in the EQUIP project. Morphological variations in overgrowths of late stage calcite have suggested that the position of the fresh/brackish-to-saline water transition zone has fluctuated both above and below its present location, but with additional observations the balance of evidence supports the predominance of an overall slight downward movement, by at most a few tens of metres, of the transition zone over time, i.e. a dominant trend over time of decreasing salinity at any point in this interval. This indicates that a hydrodynamic and hydrochemical response at 300-400 m depth to changes in the surface environment should be considered in FEPs, but also that the distributions of vertical flow directions in the groundwater system has remained fairly stable over the time period represented by the late stage calcites. Data from various instrumental methods for analysing chemical and isotopic compositions of discrete calcite growth zones suggest that the compositions of groundwaters from which they precipitated changed over time. Stable oxygen ($\delta^{18}O$) isotope data, were successfully obtained with high spatial resolution microsampling, showed that a significant component (>30%) of the present groundwater at depth (i.e. below the saline-freshwater transition zone) was potentially recharged or derived from glacial sources. However, there is no evidence that glacial-recharge has introduced highly oxidizing groundwater, as suggested by some model concepts. The patterns of variations support the concept that changes in deep saline groundwaters are more attenuated than in fresher up-gradient groundwaters. In these freshwater calcites, contents of the redox-sensitive trace elements Fe, Mn and Ce are correlated which indicates that the fluctuations in compositions are related to changes in palaeoredox conditions. Thus palaeohydrogeological information suggests that FEPs for PA should consider long-term changes of redox at relatively shallow depths, although it is also evident that the scale of change is attenuated in deeper saline groundwaters. The quantitative significance of the observed Fe and Mn variations has been studied in WP4 by geochemical modelling, which shows that absolute and relative changes in Fe and Mn concentrations have non-unique interpretations in terms of redox (Eh) values.

Samples of secondary calcite from the other UK study sites at Dounreay and Cloud Hill pose some analytical and interpretative problems because the amounts of late stage calcite are low. In both cases the calcite morphologies tend to be dominated by that of significantly older secondary calcite on which late stage calcite has precipitated as a veneer. Uncertainty in calcite morphology characterisation, coupled with the very low frequency of occurrence of conductive fractures containing late calcite mineralization within the morphological transition zone at Dounreay, means that the significance of the substantial discordance in the depth locations of the transitions of morphology of late stage calcite and of salinity in the present-day groundwater profile is interpreted with much less confidence than for samples from Sellafield. Variations of redox-sensitive trace elements (Fe, Mn, Ce) are less systematic than at Sellafield although there is a general contrast between trace element contents of shallow and deep calcites with more variation at depth. However there is too much uncertainty and lack of reproducibility in these sparse localised data to interpret reliable palaeohydrogeological information. The few stable isotope data from Dounreay calcites tend to repeat the inference from isotope analyses at Sellafield that at some stage (not necessarily the last glaciation) cold-climate water volumetrically replaced pre-existing water down to about 450-500 m depth since late stage calcites below this do not have such light $\delta^{18}O$ values.

Melechov

Although this type of site, in the centre of a domed massif, has some potentially important time-dependent FEPs that might influence scenarios, the PADAMOT methodology is not applicable for the shallow depth interval to which Melechov investigations are presently limited. As is the case for the Ratones site, methods that focus on secondary minerals, specifically calcite, are not practicable for the shallow weathering zone but are likely to become valuable in deeper investigations.

An important aspect of the Melechov massif study is that the general directions of flow paths from recharge to discharge, i.e. from the uplands of the domed massif to the incised rivers at its periphery, are fairly obvious, but the depth dependence of flow and travel times to discharge are not known at all (Rukavičková, 2001). These latter properties would be of central importance for the siting and PA of a repository situated in this sort of hydrogeological environment. The PADAMOT methodology combined with conventional hydrochemical and isotopic studies could provide valuable information about the deep parts of the down-flowing limbs of the groundwater system and about the flowpaths that converge towards groundwater discharge areas at lower elevation.

Results from interpretative modelling

Interpretative models have been developed with particular focus on the processes that are relevant to data that has been acquired in WP2 from the sites in Spain (Los Ratones), UK (Sellafield) and Czech Republic (Melechov). These models investigated the processes that link proxy data with past groundwater conditions that may reflect changes of climate or other environmental characteristics, i.e. establishing whether 'cause-effect' relationships exist. Essentially, the aim was to use palaeohydrological information to calibrate 'process-understanding' models and thus provide interfaces between palaeohydrogeological information and FEPs (features, events and processes) for scenario development in PA.

For Los Ratones, the objective was to investigate the ways that climate changes might be propagated into groundwater recharge and thence into changes in groundwater compositions and ultimately into the geochemical and mineralogical proxies. This has involved the integration of models for surface water mass balance, groundwater flow and reactive transport of solutes. The methodology allows different climatic and hydrological proxies to be interfaced with a palaeohydrogeological model which supports the construction and calibration of a groundwater model for PA with boundary conditions appropriate for future changing climate. This has been achieved in the model for Los Ratones by using the VISUAL-BALAN code to estimate time-dependent changes of recharge rate constrained by palaeoclimate information from measurements of microfaunal, pollen, isotopic and organic geochemical proxies. The evolution of groundwater compositions and secondary minerals for different boundary conditions has then been simulated with the CORE^{2D} code.

For Sellafield, the objective was to mimic the geochemical reactions that might have accounted for precipitation of late-stage calcites in fractured rock groundwater systems and to understand the significance of variations of Fe and Mn contents of secondary calcite with respect to past redox conditions in groundwater systems. Equilibrium modelling has been carried out with the PHREEQC2 code for a range of batch mixing and reaction conditions and this has been supplemented by some coupled transport and reaction modelling with the PRECIP code. The conceptual geochemical models are not unique and involve assumptions about the reactions, water mixing and pre-existing solid phases that control dissolved Fe and Mn, and about how Fe and Mn are distributed between calcite and water.

For Melechov, the objective was to understand groundwater conditions in the western part of the granite massif, using the results of a hydrogeological survey with numerical modelling of the spatial distribution of hydraulic potential, groundwater flows and travel times. This is the initial

stage in the development of a site investigation methodology that is appropriate for fractured granitic rocks in the terrain and climate of the Bohemian massif. The MENHARD code was used to construct a two-dimensional spatial model of groundwater flow. Knowledge of the hydrogeological properties from borehole testing is limited to the shallow part of the system, so modelling has tested the sensitivity of flows and travel times at greater depths to uncertainties in hydrogeological properties and infiltration.

Modelling in WP4 has made progress towards the integration of independent models of biosphere/climate, groundwater and geochemistry. Integration requires information to be transferred between the various models, e.g. recharge data from the biosphere model to the groundwater model, water flux data from the groundwater model to the geochemical model. Data for palaeoclimate, geochemical, isotopic and mineralogical proxies are needed to calibrate the models. Integration also involves expert judgement and understanding of uncertainties especially with respect to temporal and spatial variability. The possibilities and realities of integration with PA groups, especially with regard to the identification and quantification of FEPs and scenarios, are considered in the report for WP5.

Integrating palaeohydrogeological information with performance assessment

It is evident from a review of past performance assessments (PAs) that palaeohydrogeology has been used variably and patchily in PA. A generic approach is suggested for increasing the way that palaeohydrogeology can be used to support PA in the future, or at least for ensuring that information is not lost from the overall safety case.

For example, an outcome of palaeohydrogeological investigations can be envisaged whereby they would show that climatic and other environmental changes over a relevant timescale in the past have not affected the host rock formation and groundwater system at repository depth at a particular site. A more likely outcome, as exemplified by PADAMOT studies, is that there are lines of evidence with varying weights that suggest that in the past there have been some changes in certain conditions at repository depth, and in this case numerical simulations will be required to evaluate their significance for safety. In this way the potential for a change in future conditions can be recognised and explicitly addressed in safety assessments. It is emphasised that even where the potential for a change in conditions at depth is recognised, the integrity of the geosphere stability concept may not be compromised.

An effective way to channel information from palaeohydrogeology into performance assessments is by translating the information explicitly into 'external' FEPs (EFEPs). These FEPs are important in scenario development for PA because they provide information about boundary conditions of the groundwater model and about the chemical properties of the geosphere, redox, pH and salinity, to which near-field conditions and radionuclide mobility may be most sensitive. To transfer this information effectively, it is necessary to appreciate how assessment experts use the FEPs to describe scenarios and where in that process are the qualitative and quantitative interpretative models that would be constrained with palaeohydrogeological information. The proposed method of using palaeohydrogeological information requires that (i) the construction of scenarios by the assessment modelling group is done in collaboration with site characterisation experts to assess the possibilities for climate-driven disturbance of the system, and (ii) that as support for this process the interpretation of palaeohydrogeological information by the site characterisation group is more quantitative and explicit in evaluating its significance for the FEPs and the associated uncertainties.

The proposed method for considering palaeohydrogeology in PA comprises several interpretative and assessment steps. These will evaluate palaeohydrogeological information in the specific contexts of PA requirements and of scientific knowledge and models. Quantitative data or qualitative information will be the outputs from geochemical and mineralogical methods and will provide varying degrees of constraint on the past impacts of FEPs. This information

will, preferably, be placed in a chronology that enables it to be linked to the known timescales of climate-driven EFEPs that affect boundary conditions on a groundwater system.

These interpretations are likely to produce palaeohydrogeological information that relates to limited spatial and temporal intervals. They are unlikely to produce a coherent and detailed model of evolution of the whole groundwater system over the timescale of interest – the integration of the various bits of information is an interpretative task in which expert judgement inevitably has an important role. In general, interpretation of groundwater data (chemistry and isotopes) identifies the major water components in terms of their typical compositions, sources and ages. Interpretation of minerals data relates to localised geochemical conditions during a discrete interval of mineral growth (or several intervals that may or may not be contiguous). There are many sources of uncertainties in the interpretations of geochemical conditions, of time intervals for which the evidence applies, of the spatial variability, and of the relationships to groundwater movements. Expert judgement is necessary to assess the uncertainties and to consider the possibilities for alternative models. Forward modelling of geochemical processes from hypothetical or typical starting conditions may be valuable as a simplified simulation of the evolution of the real system.

This information may be directly comparable with the outputs from hydrogeological and geochemical models that are used in developing PA scenarios. This is a basis for using palaeohydrogeological information as a way of testing whether the system variability introduced by scenario analysis is appropriate for that particular site.

Summary conclusions

The full significance of the geochemical and mineralogical indicators of palaeohydrogeology, i.e. of past physical and chemical groundwater conditions has not yet been fully realised even in the most advantageous studies. These studies have shown that uncertainties, assumptions involved in 'expert judgement', and calibrations of process models, remain as substantial sources of uncertainty. Nevertheless for some sites, calcite morphologies, redox-sensitive trace elements and stable isotope ratios can provide qualitative evidence of greater or lesser degrees of stability in past groundwater conditions. This evidence should be taken into account in considering whether deep groundwater conditions will be more or less stable in scenarios of future climate changes in safety cases.

There is a need to incorporate more palaeohydrogeological information into PA in order to improve the credibility of assumptions about stability of deep groundwaters and of estimates of the likely magnitudes of impacts of external changes in scenarios. This study concludes that the most appropriate way to do that is to use palaeohydrogeology to screen and quantify FEPs that are the basis for developing scenarios to be used in PA. Logical approaches to doing this have been illustrated in this study, showing the considerable steps of data acquisition, interpretation and expert judgement that are involved in attempting to quantify information for transfer into FEPs and scenarios. The process of interpretation and expert judgement is usually carried out by means of a narrative assessment of the evidence, supported by geochemical, hydrodynamic and coupled reaction-transport modelling as illustrated in WP4. A more rigourous approach, using a structured Evidence Support Logic (ESL) model, has been exemplified here but it is likely that the conventional narrative interpretation will continue to be the most practicable approach.

Narrative interpretations have been abstracted into this report from the investigations carried out in WP2 on samples from the various study sites. The principal analytical methods that have been used and evaluated in WP2 are mineralogical, geochemical and isotopic analyses of late-stage secondary calcite. Their applicability depends primarily on the occurrence of late-stage calcite in sufficient abundance for characterisation to be analytically feasible and reasonably reliable. In general, late-stage calcite has grown and been preserved at depths below the weathering zone where groundwater compositions have been continually saturated with respect to calcite. Where

these conditions obtain, as at typical repository depths, i.e. below 100-200 m, in the rocks at Sellafield, Äspö/Laxemar and Dounreay, a remarkable amount and diversity of data may be obtainable, though abundance of secondary calcite and the feasibility of sampling are strong constraints on what can be achieved. In other geological and hydrogeological conditions, e.g. in shallow groundwater environments and at earlier stages of site reconnaissance, different sampling and analytical approaches are necessary and are illustrated by the studies at Los Ratones and Melechov.

Even in the most advantageous sampling and analytical conditions, there are substantial interpretative uncertainties associated with the assumptions made in 'expert judgement' and with calibrations of process models. Further basic research to understand the geochemical and mineralogical processes underlying the genesis of secondary calcite, the calcite morphology-salinity relationship, and the distributions of redox-sensitive trace elements in secondary minerals is required to reduce these uncertainties. Nevertheless it is evident from these PADAMOT studies that, by adopting palaeohydrogeological methods that are appropriate to the particular geological and hydrogeological conditions, important qualitative evidence of greater or lesser degrees of stability in past groundwater conditions is already accessible. This 'palaeo' evidence should be taken into account in considering scenarios of future climate changes and their potential impacts on the stability of deep groundwater conditions for repository safety cases.

Acknowledgements

Numerous contributions have been made at various stages by scientists not directly involved in the project consortium. Such contributions have comprised participation in the initial workshop (reported in Technical Report WP1), supplementary studies that address palaeohydrogeological aspects complimentary to the remit of the PADAMOT project and detailed reviews of the final reports. The organisations and individuals concerned are thanked and their support is acknowledged in each technical report to which they contributed.

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Contents

1 Introduction

1.1 RADIOACTIVE WASTES, DISPOSAL AND LONG-TERM STABILITY

Radioactive wastes are produced by nuclear power plants as a by-product of the various processes associated with the production of nuclear energy and with reprocessing of spent nuclear fuel, and in the decommissioning of redundant nuclear facilities. A range of radioactive wastes also arises from the maintenance of nuclear weapons and from the use of radioisotopes in industrial research and medicine. On behalf of wider society, representatives from governments, research organisations and academia, waste management agencies and regulatory authorities are attempting to find long-term solutions for the management and eventual disposal of such wastes.

International consensus generally accepts that deep geological repositories are the preferred option for disposal of long-lived radioactive wastes. This disposal concept is currently being considered in a number of countries and is at various stages of development, from research and national consensus building to site selection and confirmation. The concept relies in large part on the passive physical and geochemical isolation of wastes from the biosphere in general and specifically from the human environment. In this respect, the geosphere provides a low permeability barrier function by retarding the movement of any radionuclide contaminants that might eventually escape from a repository and be transported in groundwaters towards the biosphere.

PADAMOT, 'Palaeohydrogeological Data Analysis and Model Testing', is a project commissioned and funded under the European Union's 5th Framework RTD programme in nuclear fission safety (Contract Number FIKW-CT-2001-00129). The project was developed to provide a demonstration of a practical approach for the analysis of groundwater systems and the use of hydrogeological information in post-closure performance assessments for radioactive waste disposal in deep geological repositories. Such a demonstration is required as one of the biggest challenges faced by governments and waste management organisations is to gain public confidence in predictions of safety for the disposal of radioactive waste.

Part of the rationale for the safety of geological disposal is that deep emplacement in low permeability rocks will put the wastes and the engineered containment system beyond the reach of climate impacts and any associated environmental change (Figure 1). There will be greatest confidence that the engineered system and the surrounding low permeability rocks will continue to provide the 'as designed' containment if they are located in a geosphere that has inherent stability with respect to tectonic and climatic influences. Therefore the long-term safety assessment of a repository needs evidence for the attenuation with increasing depth of the impacts of climate and other surface environmental impacts, or at least evidence that any changes in the deep system that might occur at a particular location in the future will have a negligible impact on repository safety. The arguments put forward to demonstrate this stability need to be reasonable and justified for the entire period being considered in the safety evaluations, which is typically up to 1 million years, in which it is predicted that dramatic climate and associated environmental changes may impact on the earth's surface. Many of the performance assessments carried out to date have implicitly assumed that geosphere conditions at repository depth will be stable far into the future and can be based on those observed at present without considering the evidence to support or challenge this assumption. Other performance assessments have assumed stylised climate scenarios and worst case geosphere impacts as variants to the base case, thus implying a high degree of conservatism in performance assessment parameters to allow for the high degrees of uncertainty.

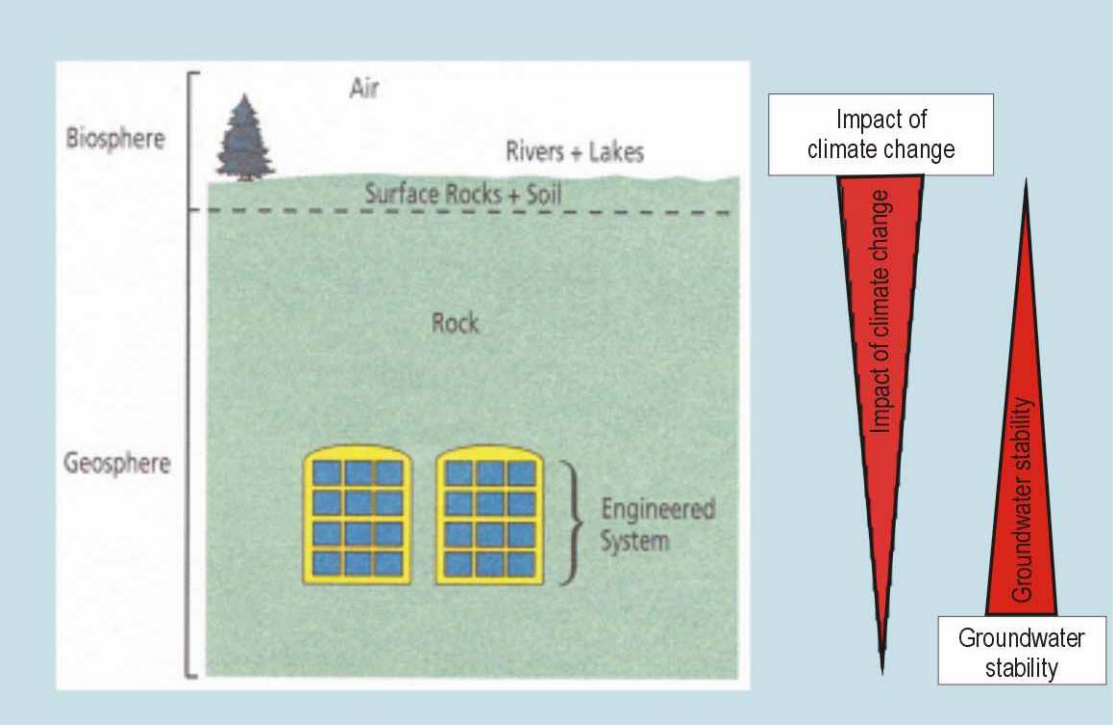


Figure 1. Isolation of radioactive wastes in a deep geological repository to take advantage of a multi-barrier system. The repository and its engineered barrier system would be constructed at a depth and location where the direct effects of any climatic or environmental change in the biosphere would be negligible and where groundwater stability could be assured.

1.2 FUTURE GEOSPHERE STABILITY AND PALAEOHYDROGEOLOGY

Scientific studies of groundwater conditions and how they have evolved to the present, 'palaeohydrogeology', can produce evidence for and against geosphere stability and to support scenarios for future changes in groundwater conditions at the location of a proposed repository. Palaeohydrogeology is also, like studies of natural analogues, a means of illustrating with hard evidence the stability, or rates and magnitudes of change, of groundwater systems over long periods of time.

There are three main aspects of palaeohydrogeology for a potential repository site:

- Numerical modelling of hydrodynamics with parameters and boundary conditions that have been set according to expert judgement of past climate impacts;
- Deductive interpretation and geochemical modelling of present-day groundwater chemical and isotopic compositions to deconvolute the 'signatures' of past infiltration conditions and the mixing of water masses that characterises past hydrodynamics;
- Characterisation and geochemical/isotopic analyses of secondary minerals and their fluid inclusions to obtain information about the groundwaters from which they were precipitated.

Essentially, palaeohydrogeological information from the interpretation of geochemical and mineralogical data is the 'hard' evidence that tests and calibrates the validity of numerical models for climate impacts on groundwaters. There is a need to develop scientifically robust and, as far as possible, quantitative ways of using that evidence to test the models, assumptions and scenarios that are used in Performance Assessment (PA). Palaeohydrogeology is also a useful means of communicating long-term safety issues and the corresponding state of understanding to both the geoscience community and to the wider public but, just as with natural

analogues, the rationale and the scientific uncertainties need to be explained clearly as a foundation for confidence building. These challenges - of supporting and communicating long-term projections in PA - were the issues that the PADAMOT project set out to address.

The palaeohydrogeological method used in PADAMOT employs observation and interpretation of data to develop hypotheses that enhance our understanding of the geosphere system. Mathematical models are then used to test the hypotheses by simulating how the natural system has developed in the past and would evolve in the future. Figure 2 shows how studies of palaeohydrogeology lead to understanding of time-dependent changes with potential impacts on repositories in the future.

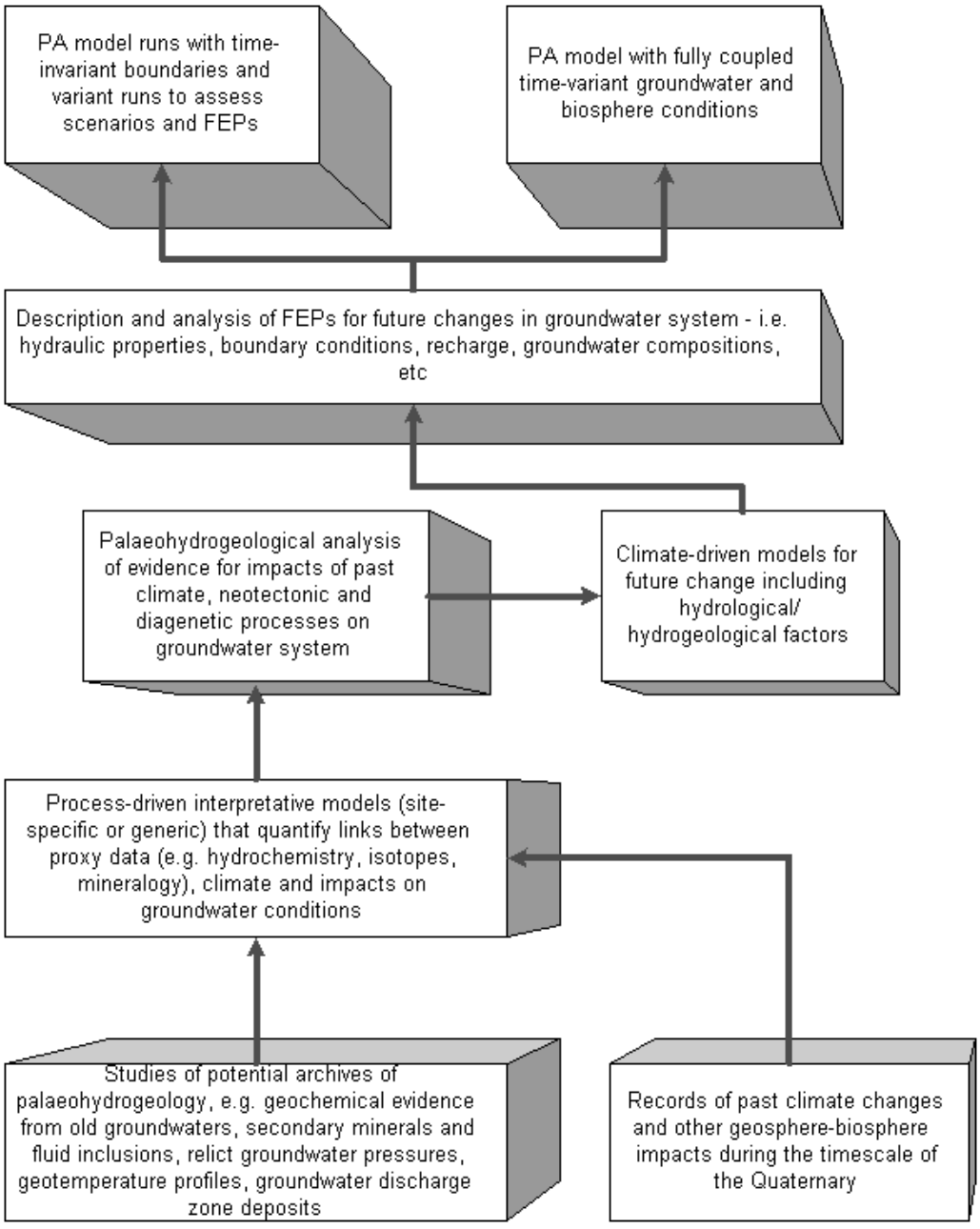


Figure 2. Logical flow chart showing how palaeohydrogeological studies combine with independent records of past climate to provide data or qualitative information (e.g. FEPs) that feed in to various approaches to Performance Assessment (PA). The intermediate stages in this process involve interpretative models that require various types of data at appropriate levels of quantification.

It also suggests the key elements in using the scientific knowledge to improve performance assessments:

- Background data – palaeoclimate, site-specific geography, geology and hydrogeology;
- New data – hydrochemical, mineralogical, isotopic;
- Interpretative models for understanding processes;
- Evidence for past groundwater conditions and analysis of uncertainties;
- Transfer concepts, uncertainties and alternatives to future time-frames;
- Produce performance assessment models that incorporate concepts and constraints.

The climate-related scenario that is generally considered to have the greatest potential impact for those sites at northern latitudes is glaciation. Theory-based concepts of how groundwater conditions change under ice sheets and permafrost and how their potential impacts should be represented in base scenarios or variant scenarios have quite large uncertainties. These are areas where additional palaeohydrogeological information would improve the basis on which scenarios are developed for northern and central European regions that will experience glacial and/or periglacial conditions in the future.

Palaeohydrogeological evidence of the past impact of glaciation has been investigated most intensively by the programmes in Sweden, Finland, UK, Switzerland and Canada. Periglacial impacts (permafrost, meltwater run-off) have also been considered by the UK, Swedish, Finnish, Canadian, Belgian and French programmes. In these countries and elsewhere, research has also been carried out at present-day cold climate sites that can sometimes be considered as analogues for past conditions elsewhere. In regions that are not susceptible to glaciation, the climatic and hydrological changes that are associated with global cycles of glacial and interglacial periods must still be considered in PA. This has been the case in Spanish and US programmes for which present-day regional climate conditions are semi-arid to arid and past conditions have included temperate to pluvial episodes.

1.3 OBJECTIVES OF THE PADAMOT PROJECT

The primary aim of PADAMOT was to investigate the evidence for or against changes in deep hydrogeological conditions over safety relevant timescales, typically considered to be up to 1 million years, and to recommend an effective way to use such evidence in safety assessments.

The specific objectives were to:

1. Review and summarise the current state of research specifically concerning the use of palaeohydrogeology in performance assessment and establish a common understanding of past practice and recent developments.
2. Hold a workshop attended by the research teams and representatives of performance assessment teams to consolidate the needs of the radioactive waste management agencies. Agree current best practise and identify how palaeohydrogeological data could be used in performance assessments. Consider the uncertainties in conceptual models and boundary conditions for numerical models of long term environmental change. Prioritise the tasks in PADAMOT according to future requirements in safety assessments.
3. Use advanced analytical techniques (e.g. ion probe, laser ablation mass spectrometry) to measure the trace element and stable isotopic compositions of individual zones in calcite samples of which some have been studied in EQUIP and some are new samples from the existing study sites. Describe past environmental changes experienced by the rocks and groundwaters and that are attributable to impacts of climate change.
4. Undertake supplementary mineralogical and groundwater analyses from new deep and shallow sites in the United Kingdom, Spain, Sweden and the Czech Republic to further investigate the effects of climate change on mineral and groundwater compositions. Train

scientists from partner organisations in the specialist analytical techniques at other partners' laboratories.

5. Obtain and interpret data that date the times of formation of fracture minerals, using isotopic methods (stable O/C isotopes and evaluation of ^{14}C and U-Th).
6. Construct a database for managing palaeohydrogeological information and for facilitating its use to support PA. Make the database accessible to all partners via internet links. Inform a wider audience (public and scientific) of the project objectives by creating an accessible web-site. Make the database publicly available at the conclusion of the project.
7. Develop and apply interpretative models that are tools for (a) understanding the processes that link the geochemical measurements that are in the database with the evolution of past groundwater conditions, and (b) estimating parameters that are required for PA groundwater models (e.g. limits on boundary conditions, travel times, redox and salinity fluctuations).
8. Deliver a recommended methodology for incorporating palaeohydrogeological interpretation in site characterisation and PA that will contribute to the demonstration of safety; this methodology will comprise scientific tools for evaluating whether or not there could be changes to groundwater conditions at repository depths and whether these would have significant impact on long-term safety. Integrate and synthesise the project results for dissemination to the scientific community in order to build confidence in the scenarios used in performance assessments.

There were some more general ambitions for the project. Waste management programmes across the EU are currently at various stages of implementation. For example, at the present time (2005), Finland is actively excavating the ONKALO underground facility at Olkiluoto as the first stage of a deep geological repository development programme. In Sweden, detailed site investigations for an underground repository are well advanced at two locations, Forsmark and Simpevarp. This progress in Nordic countries can be contrasted with the situation as found for example in the United Kingdom, where options for long-term radioactive waste management are still being considered, or Spain where a decision on long-term management of high-level waste will not be made before 2010. As well as different countries being at different stages of implementation, some differences exist in the emphasis that different national organisations give to the value of certain types of data and to the manner in which conceptual and numerical models are developed and in the way that performance assessment methods and techniques are applied. A project objective was to ensure that with regards to palaeohydrogeological data acquisition and analysis the PADAMOT partners worked together constructively to exploit and share the expertise that exists in other programmes. In this way the consortium hoped to ensure the effective transfer of best scientific practice.

There were also some technical objectives of comparing alternative analysis methods and investigating whether there were differences in the results of analyses from different laboratories using the same techniques. For example, the accuracy and precision achieved from ion probe studies (carried out at the University of Edinburgh) was compared with those from Laser Ablation Microprobe mass spectrometric analysis. The results of these inter-laboratory and analytical technique comparisons are reported in the WP2 Technical Report.

1.4 PADAMOT WORK PROGRAMME

The PADAMOT project has been driven by the need to provide methodologies, data and interpretative models for palaeohydrogeological inputs that will support safety assessments for deep geological repositories. Specifically the focus has been on investigating the degree to which the impacts on groundwater movements and compositions due to changes of climate and environment at the surface diminish with depth. The aim has been to test whether groundwater systems at typical repository depths can be considered essentially stable over long time scales, or at least to place better constraints on the degree of perturbation of groundwater conditions due to

external environmental changes when they are represented in performance assessments (see Figure 1).

The project was divided into a number of work packages, each of which was intended to build on the existing state of palaeohydrogeological knowledge and especially the outcomes of the preceding related projects in the European Union funded FP4 projects EQUIP ('Evidence from Quaternary Infills for Palaeohydrogeology'), PHYMOL ('A Palaeohydrogeological Study of the Mol Site') and PAGEPA ('Palaeohydrogeology and Geoforecasting for Performance Assessment in Geosphere Repositories for Radioactive Waste Disposal').

The work packages were as follows:

WP1. Convening a preliminary workshop of PA specialists, PADAMOT researchers and other geoscientists on the use of palaeohydrogeology in PA.

WP2. Making palaeohydrogeological data measurements on mineral samples and groundwaters from sites in Spain, Czech Republic, Sweden and UK, using high resolution and high precision analytical methods, e.g. ion probe and laser ablation.

WP3. Constructing a relational database and a public domain website to store data from EQUIP and PADAMOT, accessible to project partners and to external researchers via the internet.

WP4. Developing numerical models to test palaeohydrogeological information interpreted from proxy geochemical, mineralogical and isotopic data, based on understanding of the processes that link the proxy data with climate-driven groundwater phenomena.

WP5. Synthesising project outcomes and disseminating an improved approach to the use of palaeohydrogeological information in the description of FEPs and hydrogeological scenarios for PA.

2 The PADAMOT Study Sites

Organisations from four countries in the EU (Spain, Sweden, United Kingdom and the Czech Republic) were involved in the PADAMOT project and study sites were chosen from within the four countries so that late-stage fracture mineral and water samples could be studied from a range of groundwater systems. The locations, general geological conditions and the main reasons for studying each site are described here.

2.1 SPAIN

Three sites in Spain were studied; Los Ratones, Padul and the Cúllar-Baza Basin.

ENRESA's interest in studying the Los Ratones uranium mine site was to obtain site-specific data on shallow and deep carbonate fracture-fillings in a fractured rock in the southwest of Spain, which could potentially provide a record of the geofluid evolution in this area. The main objective was to try to determine the impact of past environmental conditions at the theoretical depth of a granitic high-level waste repository.

The strategy followed was:

- To analyse the composition of deep subsurface waters flowing through fractures because of the potential information that it can provide on the geochemical and hydrological evolution of the system. In particular, this could provide an understanding of the major chemical processes which control water composition flowing through fractures in this area.
- To determine the mineralogical and chemical composition of secondary minerals, including fracture-fillings, and to determine their spatial distribution and relationship with groundwaters. Special emphasis has been placed on characterising the carbonate minerals in the system.

The data acquired have been used for palaeohydrogeological interpretation and modelling.

The sedimentary deposits at Padul and Cúllar-Baza were studied as sources of proxy palaeoenvironmental information that could be used for time-dependent modelling of the palaeohydrogeological behaviour of groundwater systems in this part of the Iberian Massif. Earlier studies of samples from these sites were carried out in the FP4 EQUIP project. The sedimentary records have provided information that is interpreted in the context of climatic change. The Cúllar-Baza lacustrine record has information about precipitation and palaeotemperature regimes, mainly based on the analysis of the stable isotope ($\delta^{13}C$ and $\delta^{18}O$) signatures from biogenic calcite (ostracod shells). The Padul peat deposit contains evidence about palaeoenvironment from which information on past climate states and hydrology can be elucidated or inferred. In both areas a significant effort was devoted to the dating of the analysed sequences. Palaeoclimatic data obtained from these two sites was used to estimate the palaeohydrological boundary conditions at the Los Ratones site which is situated in a similar climate zone.

2.1.1 Los Ratones

Los Ratones is the site of a disused uranium mine, situated in the central southern sector of the Albalá granitic pluton in the southwest section of the Iberian Massif which is the westernmost segment of the European Variscan Belt (Figure 3a). This area has experienced fluctuating aridity and water table elevation in the past. The pluton is a concentric zoned body, elongated in a N-S direction, with biotitic, porphyritic granites in the rim and fine-grained two-mica leucogranites in

the core. Tin, tungsten, phosphate and uranium mineralizations are present in late-magmatic dykes and are genetically related with the most differentiated leucogranitic host rocks.

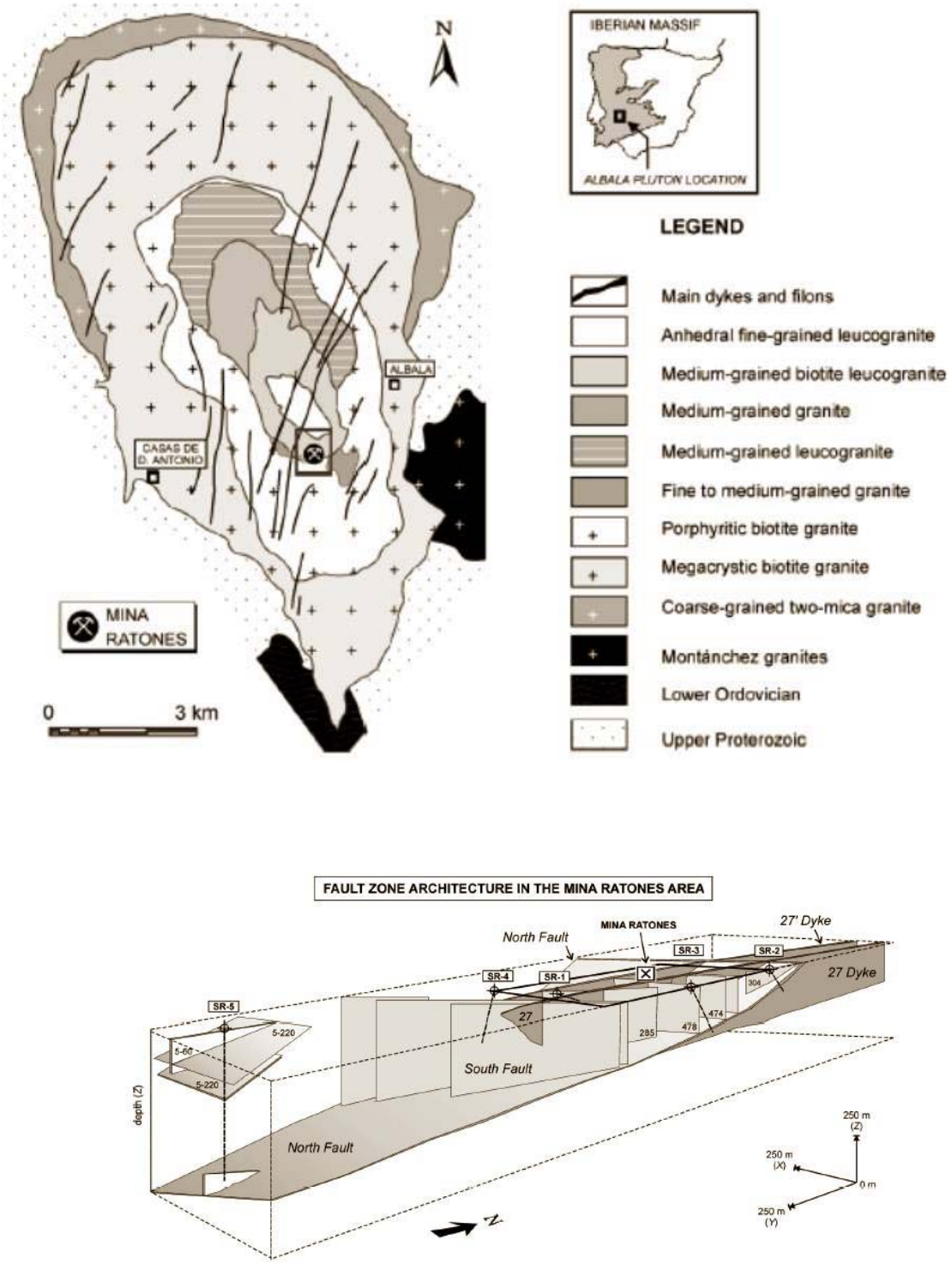


Figure 3. (a) Geological map of the Albala granitic pluton; (b) Fault architecture of Mina Ratones area (Martí et al., 2002). The main identified structures are the North Fault, the South Fault and the 27 and 27' Dykes.

The mine is situated in a topographically-controlled groundwater discharge area with flow paths mostly occurring through the upper 200 m of overburden bedrock and through the altered and fractured zones in the main structures.

Five 101 mm diameter boreholes were drilled around the mine to depths of up to 500 m. Borehole SR-1 was inclined and cut a dyke between 65 and 75 m depth. Borehole SR-2 (79 m deep) sampled waters that circulate through the Northern Fault at a depth of 58-60 m; these waters were considered to represent the recharge waters flowing into the mine. Borehole SR-3 (195 m deep) sampled groundwaters that flow at a greater depth through the Northern Fault (140-150 m), and enabled information to be gained on the chemical evolution of the water as a function of depth, between two hydraulically connected zones. Borehole SR-4 (124 m deep), located at the southern part of the mine, sampled waters from the Southern Fault which according to the hydrogeological conceptual model of the zone would have been a previous pathway for water discharge from the mine. Borehole SR-5 (500 m deep) was located to the south of the mine but was far away from the dykes and groundwater compositions in this borehole reflected the impact of the mine.

Three hydrogeological units have been distinguished:

a) Areas of superficial covering, of reduced thickness and irregular distribution, characterized by short and shallow flows and seasonal springs, and that can constitute part of the recharge and subterranean discharge of the granites;

b) Altered and fractured zones (150-200 m depth) characterized by relatively high transmissivities (10^{-4} to 10^{-6} m^2/s). The main structures and the network of minor fracturing connecting with them control the flow;

c) Fresh relatively intact granite that constitutes a low permeability media, in which the water flows through sparse fractures with a contrasted conductivity with respect to the more densely-fractured granite.

Uranium mineralization at Los Ratones comprises U silico-phosphates, phosphates, silicates, and oxides. The major development of uranium mineralization was encountered in the boreholes situated in the south of the study area (SR5, SR4 and SR1).

Dissolved U in groundwaters around the Ratones Mine varies between <1 and 10 µg/L. In general, these concentrations are low due to the reducing conditions. Higher values have been measured in some packered-off borehole sections associated directly with uranium mineralization and in the mine ventilation shaft. Overall, the distribution of U minerals present in fracture fillings correlates with high U concentrations in groundwater (Gómez et al, 1999).

The conceptual hydrogeological model for the site proposes that groundwater flow is controlled by topography to a depth of at least 200 m and that groundwater preferentially flows through the North Fault within which the main rock-water interaction processes take place. Below this depth the flows are regional and originated away from the influence of the mine. The most important water-rock interaction process with respect to the neutralization of pH in those waters affected by sulphide oxidation is the dissolution of carbonate minerals found in the fractures and dykes. Furthermore, the precipitation of siderite has a significant contribution in the regulation of Fe^{2+} and HCO_3^- in the mine waters. Ionic exchange with smectites in the fissure fillings is the main process that controls the cation concentration in the waters.

The North Fault contains little or no U mineralization, and consequently the groundwater discharging from the fault zone contains a very low concentration of U. Dissolved U present in the groundwaters in the southern part of the site is derived from reaction with U minerals in mineralized zones. Geochemical modelling of the Los Ratones water-rock reactions is described in Gómez (2002); further modelling of the system with the coupled flow-reaction model $CORE^{2D}$ has been carried out in WP4.

2.1.2 Cúllar-Baza Basin and Padul

The objective of the study of the Cúllar-Baza and Padul basins was to obtain palaeoenvironmental information to be applied as boundary conditions in modelling the palaeohydrogeological behaviour of groundwater systems in this region. The Cúllar-Baza

lacustrine archive has recorded information about precipitation and palaeotemperature regimes in the stable isotopic compositions of ostracods. The Padul peat deposit archive contains a wide range of information in fossil pollen and biomarkers about palaeoenvironment from which information on past climate states and hydrology can be elucidated or inferred. Palaeoclimatic data obtained from these two sites has been used to estimate the palaeoclimatic history at the Los Ratones site.

The Cúllar-Baza (Guadix-Baza) Basin is a 'basin and range' endorheic depression that covers approximately 4500 km^2. It is located in the central part of the Betic Range (Figure 3), in the northeast extreme of the Granada Province (Andalusia, South-eastern Spain). It has an irregular shape with its maximum length oriented SW-NE and is at an elevation of 900-1000 m a.s.l.

The origin of the basin is related to the Alpine orogeny which affected Mesozoic and Cainozoic rocks within the region. The bedrock comprises mainly Mesozoic limestones, dolostones, marls and gypsum, and Neogene sediments of marine origin. Later, during the late Miocene, the sedimentary conditions changed to a continental regime.

In brief, the basin can be understood within a centripetal depositional model: consisting of coarse grained alluvial fans at the foot of mountain ranges, which gradually pass into a system of channels that flowed out to a central system of small shallow saline lakes distributed in a mosaic pattern with sedimentation of gypsiferous lutites, gypsiferous sands, gypsum and, sometimes, decimetrical lutite beds with displacive gypsum crystals. At the end of Middle Pleistocene, erosive processes began and the current fluvial system was established, producing the typical badlands landscape that can be observed today.

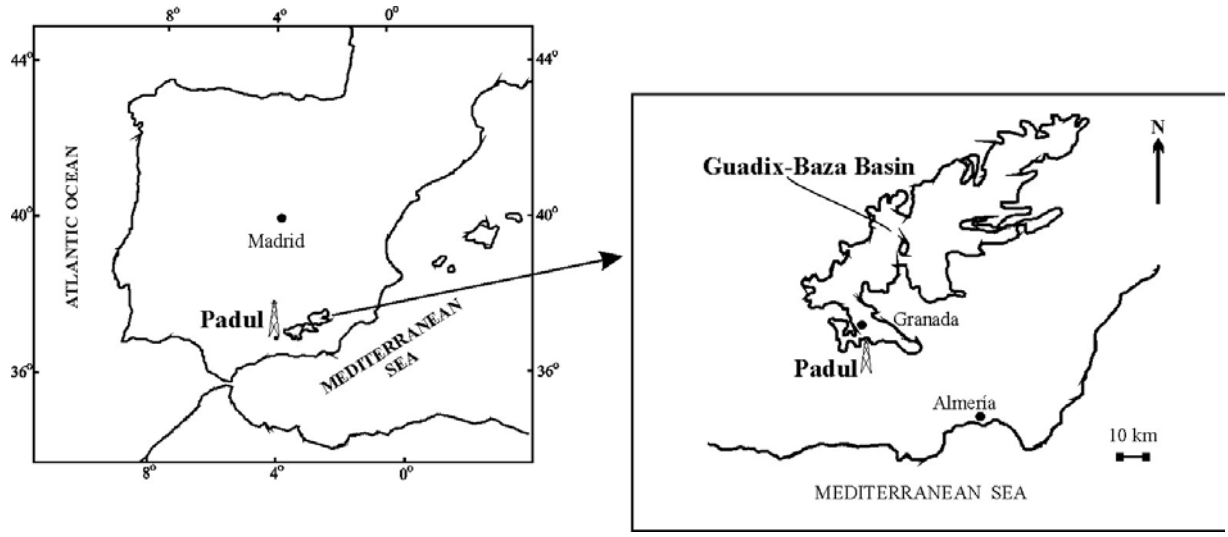


Figure 4. Location map of the Padul peat deposit and the Cúllar-Baza Basin

The Padul peat deposit is located 20 km south of Granada (Andalusia, southern Spain) (Figure 4). It was formed in a depressed fault-bounded tectonic basin at the foot of the Sierra Nevada, and consists of an endorheic basin, surrounded by mountains. It has an elevation of 720 m a.s.l. and some parts are permanently covered by water. Its longitudinal axis is NW-SE oriented, and it has a surface area of 4 km^2 and a maximum depth of 100 m. The bedrock consists mainly of faulted Mesozoic dolostones that caused the basin to sink gradually.

The Padul Basin is a discharge area for groundwater flow from the surrounding aquifers. The flow directions change from sub-horizontal, in the Mesozoic aquifers adjacent to the basin, to an essentially upwards discharge inside the peat-containing depression.

The lowermost part of the stratigraphic record begins with very immature and poorly cemented conglomerates of alluvial origin, followed by lacustrine marls with some sandy/conglomeratic interbeds of fluvial origin as well as peat seams. The marls may or may not be cemented and their terrigenous content is highly variable. The organic matter content of the marls is also very variable: scattered phytoclasts, carbonaceous particles or simple specs, and grey organic-rich beds. Lamination, if developed, has not been preserved due to bioturbation. The uppermost part of the Padul peat sequence is massive peat with some marly intercalations.

2.2 SWEDEN

The Swedish study site was Laxemar which is situated on the Baltic coast of southeast Sweden (Figure 5). Together with the adjacent Simpevarp area and Forsmark, the site is currently being investigated by the Swedish Nuclear Fuel and Waste Management Company (SKB) as a prospective location for a spent fuel repository. SKB have an underground hard rock laboratory (HRL) on the nearby low-lying island of Äspö (Figure 5) where it is carrying out a programme of investigations to develop and test methodologies for research into the storage of spent nuclear fuel.

The bedrock of the Laxemar-Simpevarp-Äspö area is characterised by intrusive granitoids belonging to the Transcandinavian Igneous Belt with ages of around 1.8 billion years. The rock compositions range from quartz monzodiorites to granite.

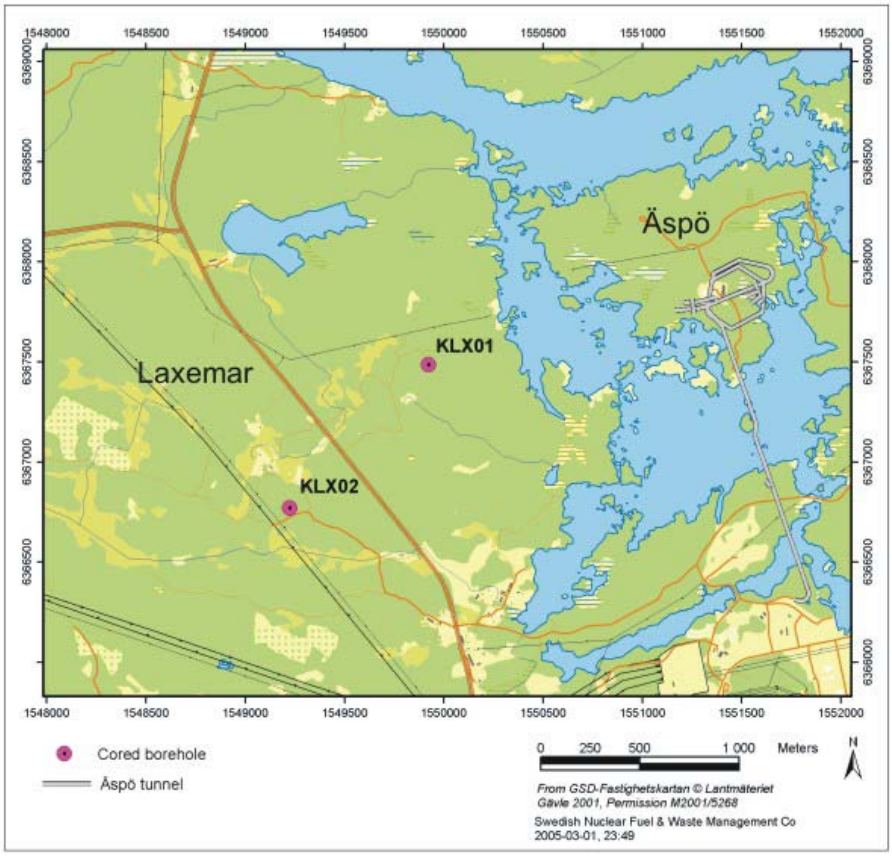


Figure 5. Map of the Äspö and Laxemar area showing the location of site investigation boreholes.

PADAMOT investigations were based on drillcores from borehole KLX01, which was drilled down to 1070 m depth at Laxemar on the mainland west of Äspö prior to excavation of the HRL. The FP4 EQUIP project obtained palaeohydrogeological information from borehole cores in the Äspö area. SKB's study has focused on late-stage secondary calcite mineralization because of

the potentially wide range of different analytical information (petrographical, morphological, microchemical, stable C and O isotope, Sr isotopes, fluid inclusions) that can be obtained from this mineral. However, a major problem had to be faced in that the amount of calcite present in any given fracture is usually very limited even though it occurs in many of the open fractures.

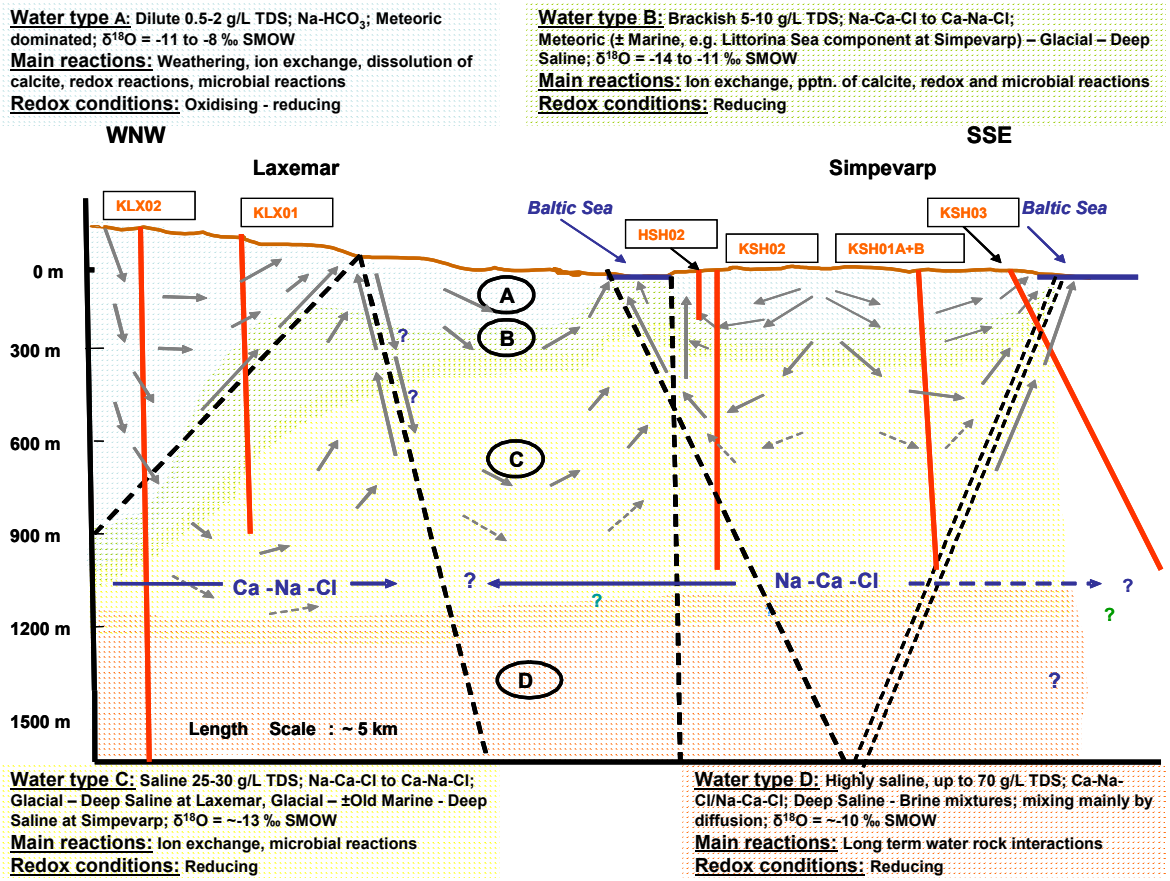


Figure 6. Conceptual model of the groundwater chemistry of the Laxemar/Simpevarp area (from SKB, 2004). The situation at Äspö is similar to Simpevarp (see Figure 5)

The strategy for the investigation was:

- To use the morphology of late-stage calcite for selecting the most recent and low temperature calcites;
- To combine different types of analyses on these calcites including $\delta^{18}O$, $\delta^{13}C$, $^{87}Sr/^{86}Sr$, chemical composition (including trace elements) and fluid inclusions, in order to interpret possible past hydrogeochemical regimes and influences of the surface and shallow environment on deeper groundwaters (such as input of organic or biogenic material).

The most recent influence on the stability of the groundwater system in these low permeability fractured rocks has been the several episodes of ice sheet cover and associated periglacial effects during the Quaternary period. Mechanical loading by the ice sheets depressed the underlying crustal rocks and the hydraulic effects of meltwater in the ice sheet and of interglacial permafrost formation were potential influences on groundwater. Since the end of the last glaciation about 10,000 years ago, the land surface has been rising due to crustal rebound and consequently the shoreline has been receding.

Present-day groundwater compositions across the Laxemar/Simpevarp/Äspö area, and the inferred groundwater flow directions and palaeohydrogeological water sources, are shown in Figure 6.

The palaeohydrogeological objective was to better understand how these glacial and postglacial environmental processes have affected shallow and deep groundwater conditions.

2.3 UK

Samples from three UK sites were studied: Sellafield, Dounreay and Cloud Hill. PADAMOT studies have built on data from the FP4 EQUIP study of samples from Sellafield and to extend the approach to other UK sites. The overall aim has been to test whether the palaeohydrogeological relationships between the characteristics of late-stage secondary calcite and groundwater chemistry, as observed at Sellafield, could be applied more generically.

2.3.1 Sellafield

The Sellafield study site is located on the Cumbrian coast of northwest England (Figure 7). The site was investigated by Nirex between 1989 and 1997 to determine whether the site would be suitable to host a deep geological repository for intermediate- and low-level radioactive waste. Twenty-nine boreholes (mostly cored) were drilled by Nirex within an area of 8 km by 6.5 km, the deepest borehole (BH3) reached 1950 m depth (Figure 8; Nirex, 1997a). Detailed petrological studies have been made of the fractures and associated mineralization encountered in twenty-three of these boreholes. Analyses of the Sellafield borehole cores were previously carried out in the FP4 EQUIP project.

Sellafield lies on a moderately flat coastal plain, about 10 km wide and is bounded to the west by the Irish Sea and to the east by the uplands of the Lake District, from which it is separated by the Lake District Boundary Fault Zone.

The bedrock geology consists of an eastwards-thinning wedge of Permo-Triassic sedimentary strata, which overlap Carboniferous rocks resting on Lower Palaeozoic rocks of the Lake District Massif (Figure 8). The sequence of Permo-Triassic sedimentary rocks comprises the Triassic Sherwood Sandstone Group with a basal conglomeratic or breccia unit (the Brockram). These directly overly basement in the eastern and central parts of the site, being about 400 m thick in the central part. In the western part of the site, the sandstones are separated from basement rocks by Permian mudstones and evaporites and Carboniferous rocks. The Permo-Triassic sequence thickens rapidly westwards beyond the coast into the East Irish Sea Basin where it attains a thickness of several thousand metres. The basement rocks are regionally-metamorphosed lavas, pyroclastic and volcaniclastic rocks of the Lower Palaeozoic Borrowdale Volcanic Group which can be considered to be a fractured crystalline rock with low permeability.

The most recent period of tectonic change in the East Irish Sea Basin involved uplift and erosion during the Tertiary period, after which the basinal area was inundated by the Irish Sea. This region of northwest England has been glaciated several times during the Quaternary period. Much of the Sellafield area is blanketed by a variable thickness of unconsolidated tills and interbedded glaciofluvial and glaciolacustrine deposits, largely attributed to the latest (Devensian) glaciation.

Petrological studies show that the shallow and deep groundwater flow paths have evolved over time. Much of the fracture porosity is secondary in origin, having been rejuvenated by the dissolution of geologically old vein minerals, principally anhydrite and dolomite-ankerite (and also calcite at shallow levels) belonging to earlier mineralisation. The post-uplift (Tertiary) enhancement of secondary porosity is progressively developing westwards and down-gradient from the recharge area as dissolution proceeds. Porosity enhancement is offset to a lesser extent by porosity reduction through the precipitation of secondary late-stage calcite mineralisation. As a result of this process, the porosity/flow pathways in the east of the site are likely to be older and more evolved, and they progressively become younger and less evolved westwards.

This evolution is reflected in the growth fabric of the late-stage calcite mineralization, which

precipitated from the groundwater as it became supersaturated with respect to calcite down-gradient, or as invading meteoric water mixed with relict water in the host rock. Calcites in the east of the site display the most complex sequence of up to eight late-stage growth zones, representing a more fluctuating and possibly longer evolutionary history. By contrast, at the west of the site there are only up to four growth zones, representing a shorter or less complex evolutionary history. Geochemical data support a close relationship between the evolution of the fracture system and late-stage calcite precipitation. Early growth zones in the calcite are often enriched in Mg, which is consistent with the dissolution of early stage dolomite-ankerite mineralization. This is particularly notable in the shallow system where the effects of dolomite-ankerite dissolution are greatest.

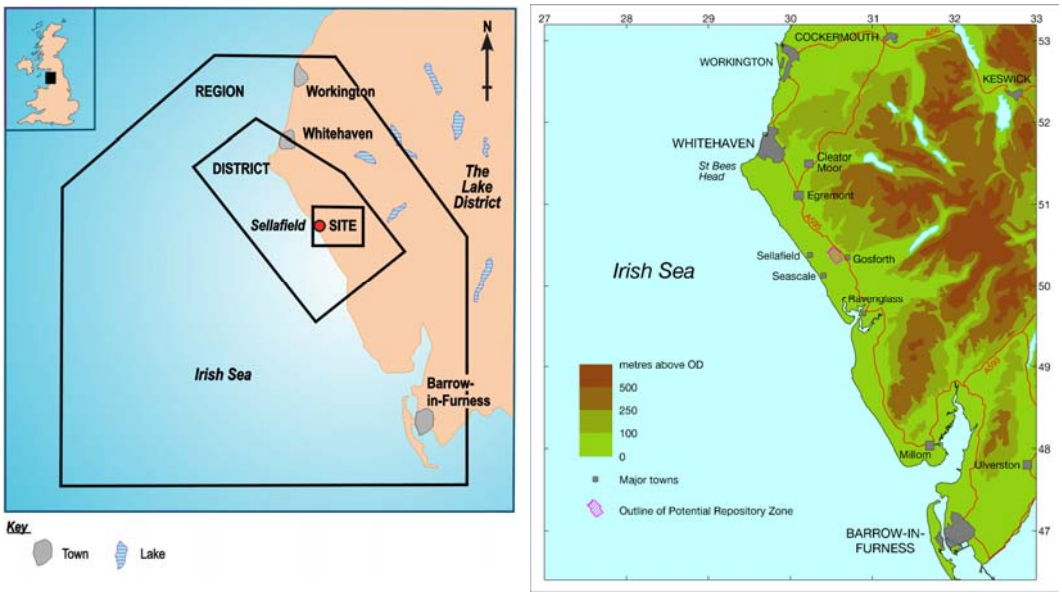


Figure 7. Location of the Sellafield study site and illustration of the regional topography.

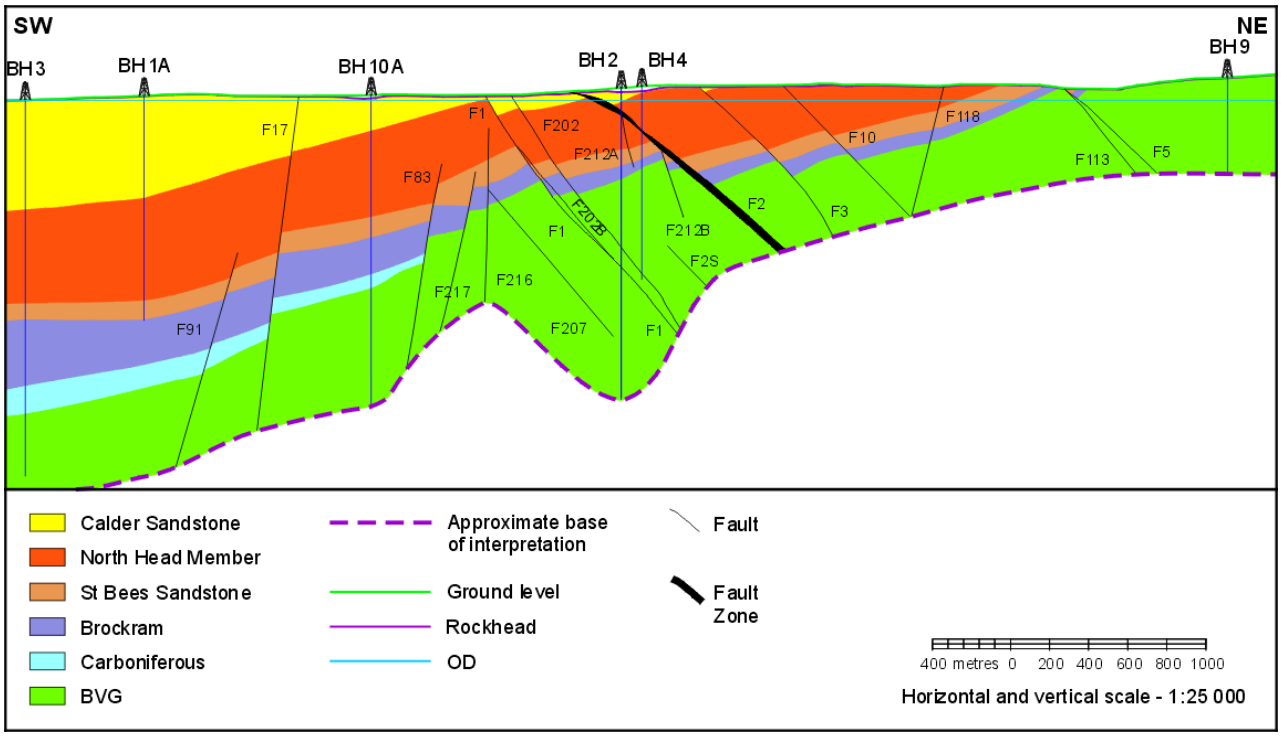


Figure 8. Geological NE-SW cross-section of the Sellafield area.

Groundwater compositions change with depth at Sellafield with a sharp increase in salinity occurring at about 300-350 m depth in the centre of the investigated site, where shallow circulating fresh water interfaces with deeper saline groundwater in a 'Saline Transition Zone' (STZ).

The conceptual model of the groundwater system of the Sellafield region comprises three discrete regimes: (i) Fresh to brackish groundwater in the coastal plain in which flow is topographically driven and recharged directly; (ii) Halite-derived brines from the Irish Sea Basin, occurring at depth in the western part of the site beneath the present coastline; (iii) Groundwater in the hills to the east of the site and in the basement within the site in which flow is topographically driven with the additional effect of density variations in deep saline groundwaters. The movement of interfaces between these bodies of groundwater at Sellafield is symptomatic of the hydrodynamic evolution and stability of the groundwater system and also might have affected its geochemical stability.

2.3.2 Dounreay

Dounreay is located on the Caithness coast of northeast Scotland, about 12 km west of Thurso. The site was investigated by Nirex between 1989 and 1991 to determine whether it would be suitable to host a deep geological repository for intermediate- and low-level radioactive waste (Nirex, 1994). Two boreholes were drilled and cored at Dounreay, the deepest (BH1) reaching a depth of 1327 m, penetrating 375 m of Devonian sedimentary rocks and 950 m of crystalline (mainly psammitic) metamorphic and igneous rocks (Figure 9). Investigations during this study have focussed on drillcore samples from borehole BH1.

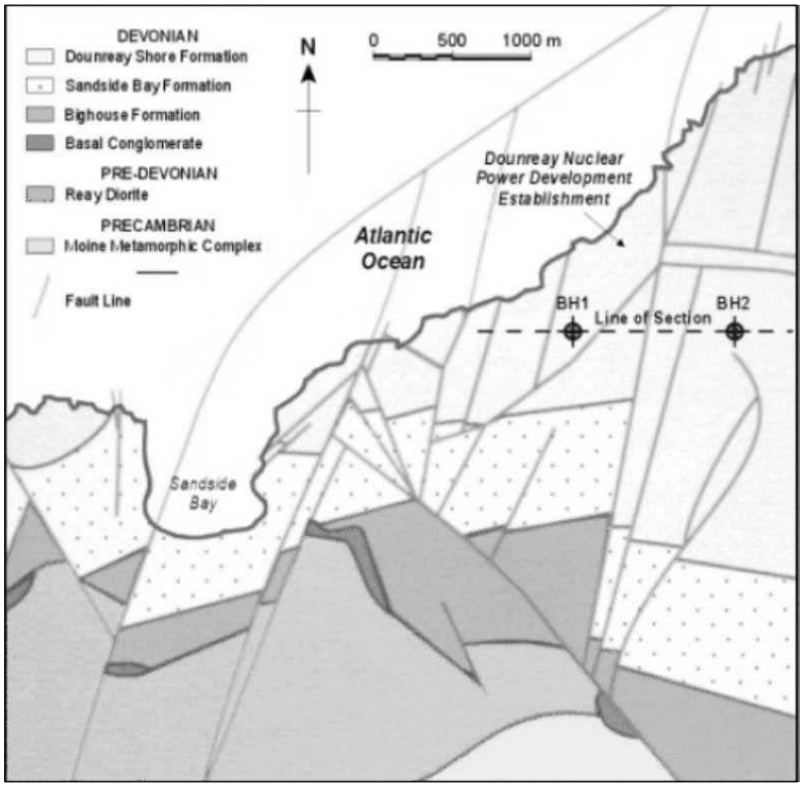


Figure 9. Geological Map of the Dounreay area showing the location of deep boreholes.

Dounreay lies on a relatively narrow coastal plain underlain by Devonian sedimentary strata and, beneath them, crystalline basement rocks. The outcrop of Devonian rocks extends 2 to 3 km to

the south of the site and merges with a series of low peat-covered hills with isolated outcrops of basement.

The Devonian sedimentary rocks were largely deposited in the Orcadian Basin developed after the Caledonian Orogeny. The strata comprise patchily developed Lower Devonian sandstones, siltstones and conglomerates that are unconformably covered by Middle Devonian sediments, consisting of a thin basal conglomerate, medium to coarse sandstones and finely bedded lacustrine rocks of the Caithness Flagstone Group which dominate the basin fill. Between 300-600 m of Caithness Flagstone Group strata are present in the Dounreay area.

The crystalline basement rocks comprise a complex series of Precambrian metasedimentary rocks (dominated by migmatitic psammites) generally correlated with the Moine assemblage (Moine Supergroup). These are cut by two major igneous intrusions, the Strath Halladale Granite and Reay Diorite.

This area was covered by ice sheets several times during the Quaternary period, but the extent to which the Dounreay site was glaciated during the Devensian is unclear. The present-day land surface is covered by drift deposits, predominantly peat and glacial till. These tills are considered by some authors to have been deposited by the earlier 'Wolstonian' ice whilst other authors argue that they are Late Devensian. If indeed the tills are Wolstonian, then their preservation suggests that Dounreay may not have experienced significant ice cover during the Devensian.

Groundwater flow is predominantly fracture-controlled in both the crystalline basement rocks and in the overlying Devonian sedimentary cover rocks. The Devonian strata thin rapidly southwards and the crystalline basement rocks form low outcrops rising to 200 to 300 m OD. The principal groundwater flow direction is from south to north, with recharge in the low hills to the south of the site. The groundwater is considered to flow northward and downward, along bedding-related and fault-related fractures, to a zone of discharge and upward flow in the Dounreay coastal plain and possibly offshore.

Only limited data are available on the groundwater chemistry at Dounreay (Nirex, 1994). The salinities are relatively low down to about 750 m depth, but below this salinities progressively increase to about 10,000 mg/L TDS at c.1150 m.

2.3.3 Cloud Hill

Cloud Hill is one of a number of Carboniferous Limestone inliers in northwest Leicestershire, in the East Midlands of England. Samples were collected from the base of a large quarry in fractured dolostone and limestone that is being worked for aggregate. The sequence is highly fractured and extensively dolomitized and is unconformably overlain by red-bed mudstones and siltstones of the Triassic Mercia Mudstone Group. The Carboniferous strata have been affected by karstification, probably of Permo-Triassic age, beneath the unconformity.

The highest point of the site, on the eastern face of Cloud Hill Quarry, has an elevation of 111 m, and the bottom of the quarry is at about -10 m elevation. Groundwater in the Carboniferous Limestone is most probably recharged locally and discharges from open fractures in the base of the southern end of quarry in which late-stage calcite was found. Samples of this late-stage calcite mineralization, plus groundwater from the same fractures, were collected and analysed.

2.4 CZECH REPUBLIC

The Melechov Massif is a Variscan granite body located about 80 km to the SE from Prague and is the northernmost promontory of the Moldanubian pluton in the Bohemian Massif (Figure 10). The area is being used for testing methodologies for the development of a deep geological repository in crystalline rock. The objective of PADAMOT studies at Melechov has been to

clarify and update ideas about the shallow origin and circulation of groundwater in the fractured granite and to provide data for hydrogeological modelling.

The region has a complex system of fractures and fracture porosity, related to its long and complex tectonic history. In addition, Tertiary uplift and erosion have significantly modified the land surface and impacted on drainage patterns. Furthermore, weathering and superficial deposits affect the permeability of the fissured zones. These features seem to be the controlling factors on groundwater circulation and residence times. A general investigation objective is to find out if there are deep groundwater circulation systems in tectonic zones and to compare groundwater residence times in fissures with residence times in granites elsewhere in the Bohemian Massif.

Petrological, mineralogical and hydrogeological information was obtained from borehole PDM-1 which was drilled at 122 mm diameter to 100 m depth at the southern foot of Melechov Hill in 2002. A hydrogeological field survey was also undertaken to provide input data for hydraulic modelling of the groundwater flow system. Sixty groundwater samples were collected and analysed in the chemical laboratory of the Czech Geological Service.

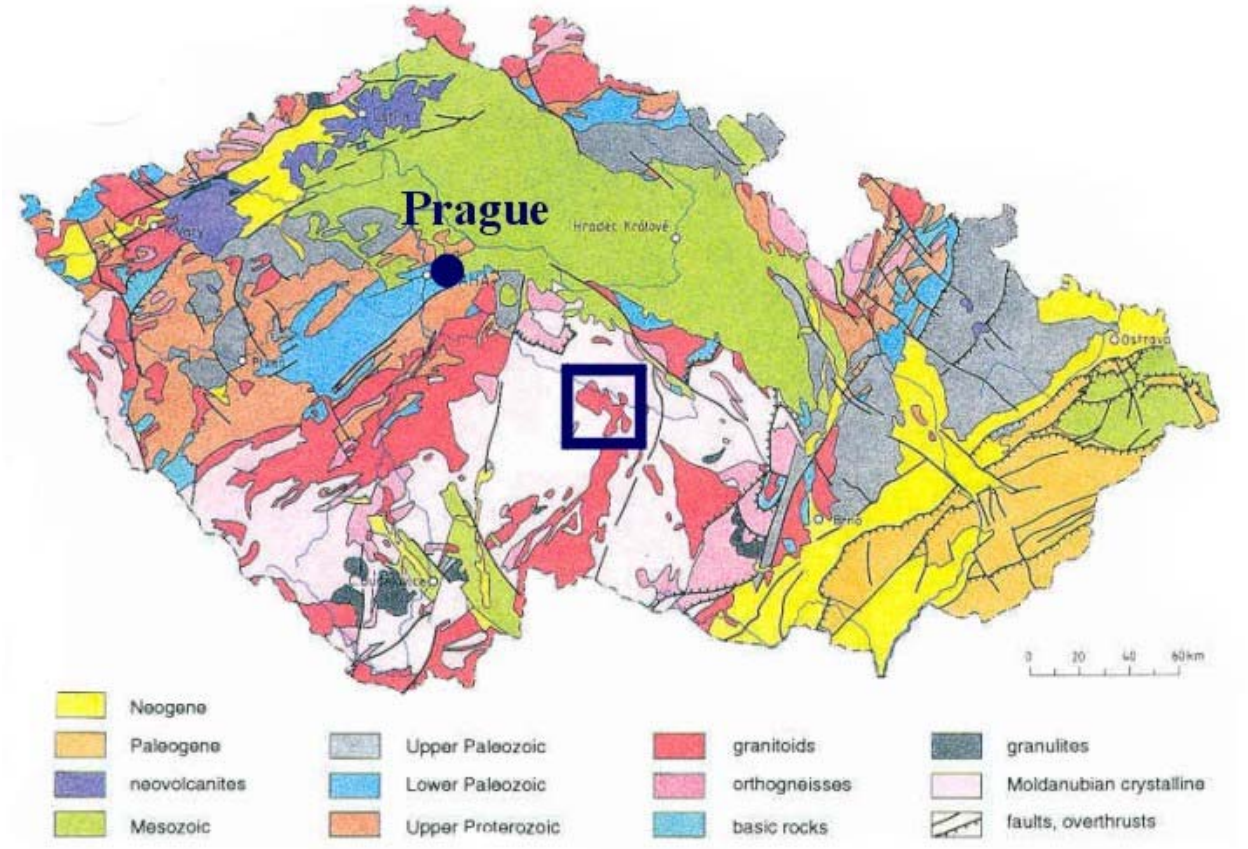


Figure 10. Geological map of the Bohemian Massif. The position of the Melechov Massif is highlighted by the thick square.

There are two main fracture systems at Melechov: an older fracture system oriented NNE-SSW inclined towards the centre of the massif, and a younger subvertical system oriented WNW-ESE (Mlčoch, 1994, Mlčoch et al., 2000a,b). There is an especially good relationship of geological boundaries and the courses of rivers with the orientation of the younger fracture system in part of the massif. Groundwater flow is mostly related to fracture porosity, which is dependent on fracture occurrence and connectivity of single fractures. Only in the uppermost part of the massif (the weathered mantle) can mixed porosity be found. The thickness of this mixed

porosity zone can reach a maximum depth of 30 m, depending on the intensity of erosion, topographic position, etc. Values of hydraulic conductivity determined by pumping tests vary from 10^{-6} to $4x10^{-5}$ m/s (Rukavičková, 2001). These values represent only the shallow part of the massif (maximum depth 30 m); deeper values are not known because of the absence of deep boreholes. The magnitude of hydraulic conductivity is related to the thickness of weathering, topographic position and of course on fracture occurrence, and does not depend on geology.

3 WP1: Workshop on Palaeohydrogeology in Performance Assessment

3.1 INTRODUCTION

An international workshop was held in Brussels in October 2002. The workshop was attended by approximately 40 people: researchers from the PADAMOT consortium, by Performance Assessment (PA) modellers and by other geoscientists with experience in palaeohydrogeology, specifically some of those who had worked in the FP4 projects EQUIP, PAGEPA and PHYMOL.

The general objective of the workshop was for the PADAMOT partners to improve their understanding of the 'state of the art' as exemplified by the results of the FP4 projects and of the PA requirements for information from palaeohydrogeology.

The specific workshop objectives were to:

- Consider evidence that is relevant to considering long-term stability in the chemical and hydrogeological environment at typical repository depths;
- Identify generic and site-specific data and interpretations that improve understanding of long-term groundwater conditions at repository depth;
- Review how palaeohydrogeological evidence for the evolution of groundwater conditions has been used in safety assessments for deep geological disposal;
- Propose new methods for incorporating palaeohydrogeological knowledge into safety assessments.

The workshop presented up-to-date views of investigation techniques, the types and accuracy of data that can be obtained, the uncertainties in these data, and the methods for integrated interpretations that can be effectively used in PA. Independent expert 'facilitators' and rapporteurs were then used to synthesise and report issues, especially those relating to the value and use of palaeohydrogeological information in repository safety assessments.

A pdf file of the report for WP1 is included on the CD-ROM at the back of this report:

> The Long-Term Stability of Groundwater Conditions at Repository Sites: Proceedings of the PADAMOT Workshop, Brussels 2002. A Bath, G Boulton, A Bowden, P Degnan, T McEwen, A Milodowski, J Smellie, I Wemaere. (Editors: A Bath, P Degnan, M Gillespie). PADAMOT Project Technical Report WP1. 89 pp. January 2003.

3.2 DAY ONE: REVIEWS

The first day of the workshop comprised invited overviews of palaeohydrogeology projects in the EC's 4th Framework Programme (FP4), namely EQUIP, PHYMOL and PAGEPA and the investigation at Palmottu in Finland (summary in Bath et al., 2000b). In addition to these summary papers, an introduction to the PADAMOT project and a brief synopsis of the potential use of novel analytical techniques for future palaeohydrogeological studies were presented.

EQUIP developed geochemical and mineralogical techniques for palaeohydrogeological study (Bath et al., 2000a). This type of geochemical/mineralogical approach and the complementary hydrochemical/isotopic studies on groundwater samples are the only sources of primary data for palaeohydrogeology. Isotopic and organic geochemical proxies for palaeoclimate and

palaeohydrology in surface water and shallow groundwater regimes in semi-arid southern Europe were also demonstrated.

PHYMOL developed the use of groundwater isotopic data for palaeohydrogeology, specifically for calibrating a hydrodynamic model of the region around Mol in Belgium (Marivoet et al., 2000). Independent palaeoclimate information was used to estimate time-dependent boundaries and initial conditions for a hydrodynamic model which then transported the isotopes in a forward model to reconstruct present-day conditions. Comparison of observed with modelled isotope data tested the model which was then used for a PA calculation of radionuclide concentrations in aquifers either side of the clay host formation.

Numerical hydraulic models were developed in PAGEPA and were further developed in the BENCHPAR project to simulate the processes in groundwaters overlain by, or adjacent to, ice sheets (Boulton et al., 2001). Amongst the phenomena modelled are infiltration of glacial meltwaters, discharge through ice tunnels or eskers, permafrost, and overpressuring due to loading. Water movement must be modelled in 3-dimensions to represent the geometrical heterogeneity of these phenomena. As modelling gets more complex, so the requirement for modern analogue and interpreted palaeohydrogeological evidence gets more demanding.

The Palmottu site in Finland is a U-mineralized natural analogue site for which intensive study has added substantial knowledge about hydrogeology and palaeohydrogeology of Fennoscandian crystalline rocks (Blomqvist et al., 1998). Groundwater chemistry and isotope measurements have been supplemented by fracture mineral studies. U-Th dates for secondary calcites are correlated with interglacials, i.e. mineral growth during wet periods. As with EQUIP there was a significant amount of interpretative uncertainty, but this study exemplified both the conceptual and quantitative importance for groundwater models of incorporating geochemical data and palaeohydrogeological interpretation.

There are three strands to the PADAMOT project. The first strand is the continuing development of analytical techniques which are revealing the geochemical archive of past groundwater conditions in secondary minerals. In particular, new instrumentation is being used which offers the possibility of calibrated microanalyses of isotopic and trace element compositions in individual growth zones of secondary minerals. The second strand is the construction of a database which will collect together a wide range of data types in appropriate formats for use in interpretative modelling. The third strand is the use of numerical models to simulate groundwater flow and reactive solute transport to test hypotheses for palaeohydrogeological processes inferred from the results of analytical studies.

The rapporteurs presented their commentaries on the general approach to, and value of, palaeohydrogeology as starting points for discussion. Two particular aspects were considered: (i) the data sets from site investigation and the lines of palaeohydrogeological evidence that constitute a potential input to Performance Assessment, and (ii) the extent to which such data and lines of evidence actually have been used in existing PAs. The conclusion drawn is that this type of evidence has so far been used very variably in site characterisations and PAs, and has not really achieved the potential value that had been expected and promised. However the breadth of the topic, and the conceptual overlaps with many other scientific aspects of site characterisation, mean that its value is often implicit in the way that models of groundwater systems are constructed and justified, even if it is not explicit and ‘up front’. A number of reasons have been put forward for this, but the most prominent ones seem to be the ambiguities and problems of extracting information that is quantitatively usable by PA and especially the often-subjective way that uncertainties are handled in that process. Nevertheless, the view was put forward that palaeohydrogeology provides the only sound scientific basis on which to prioritise data collection and to build a safety case. Accepting this view leads to the recommendation that more emphasis and effort needs to go into improving the ways that we tackle interpretation, uncertainties and communication of results, and also improving the balance between short and long timescales in our scientific strategy.

3.3 DAY TWO: LOOKING FORWARDS

On the second day, three working groups were constructed from the workshop participants. Each group included people with a range of skills and organisational representation. Each group addressed the same following questions:

- How do hydrochemical & mineralogical data support confidence in deep repository stability?
- How can that knowledge be applied more effectively in future safety cases?

Discussions among the working groups were focused on how the present states of expertise and knowledge in palaeohydrogeology could be taken forward to improve future value of this approach. Two directions of discussion were tackled: (i) how scientific methods, data and uncertainties relate to the concept of groundwater stability, and (ii) how the knowledge gained from these studies can used effectively in PA. There was apprehension about trying to be prescriptive about a definition for stability when there are so many site-specific factors and also variability in the dependence of multi-barrier containment on geosphere stability for different repository designs, locations and safety cases. Whilst there are many steps that need to be taken (and are already being taken) to improve the interaction and iteration of data and safety implications between site characterisation staff and PA teams, it was also recognised that we should ensure that wider public concerns about safety scenarios and timescales are given adequate attention. Palaeohydrogeology is one of the tools to address those concerns, but a more consistent and rigourous approach to evaluating evidence coupled with more innovative methods of communicating concepts, implications and uncertainties will be required.

Some of the suggestions that came out of the discussions were:

- More focus on potential impacts (or positive evidence of negligible impacts) of permafrost in northern and central Europe;
- Field investigations of processes (especially ones that are time-dependent and/or localised) that are associated with present-day ice sheets;
- Further studies to investigate the palaeohydrogeological significance of isotopic and organic geochemical proxy indicators in sedimentary sequences representing the Quaternary pluvial/arid climate cycles of southern Europe;
- Wider use of a range of timescales, e.g. 1,000 and 10,000 years, to focus research aims and to communicate safety-relevant understanding;
- Continuing development and exploitation of analytical techniques to improve primary data in areas such as the chronology and compositional variations in secondary minerals;
- Interactions between PA teams and palaeohydrogeology researchers that are focused on specific issues, for example by a structured process of constructing and testing ranges of alternative models and scenarios;
- Adopting a broad approach to discussing groundwater ‘stability’, rather than trying to be prescriptive, so that the many relevant aspects of this issue and the associated uncertainties can be considered realistically.

Finally, it was recommended that there could be a more strategic use of palaeohydrogeological research in conjunction with other research initiatives. For example, it is now more widely recognised that palaeohydrogeological studies are only one component in a ‘timeline’ of understanding that includes insights from natural analogues and model projections of future biosphere scenarios (Figure 11).

Palaeohydrogeology by its nature concentrates, through geochemical and mineralogical analyses, on understanding past groundwater movements and hydrochemical evolution. Many studies of natural analogue sites, on the other hand, investigate processes that are active. Knowledge of

past conditions is however required in natural analogue studies to properly understand present day conditions, although the emphasis may be different from explicit palaeohydrogeological research. With knowledge of past and present conditions derived from palaeohydrogeology and natural analogues, we have the potential to extrapolate our understanding into the future. Because of uncertainty, such projections can never scientifically be called predictions, but they do allow us to construct defensible scenarios. Climate change is likely to be one of the major factors in disrupting future surface and near-surface environments, for which the FP5 BIOCLIM project has constructed defensible scenarios of future climate change over the timescales of interest for repository safety assessments. That project has also investigated the potential radiological impacts of transitions between climate states, as opposed to what radiological impacts might be expected under different, but steady state, climate conditions. Outcomes from BIOCLIM and other studies that are based on palaeohydrogeological understanding and information derived from natural analogues should help to constrain scenarios of future environmental change on the surface and in the near surface. As such they will provide appropriate boundary conditions for models of the deep geosphere, where the effects are expected to attenuate with depth.

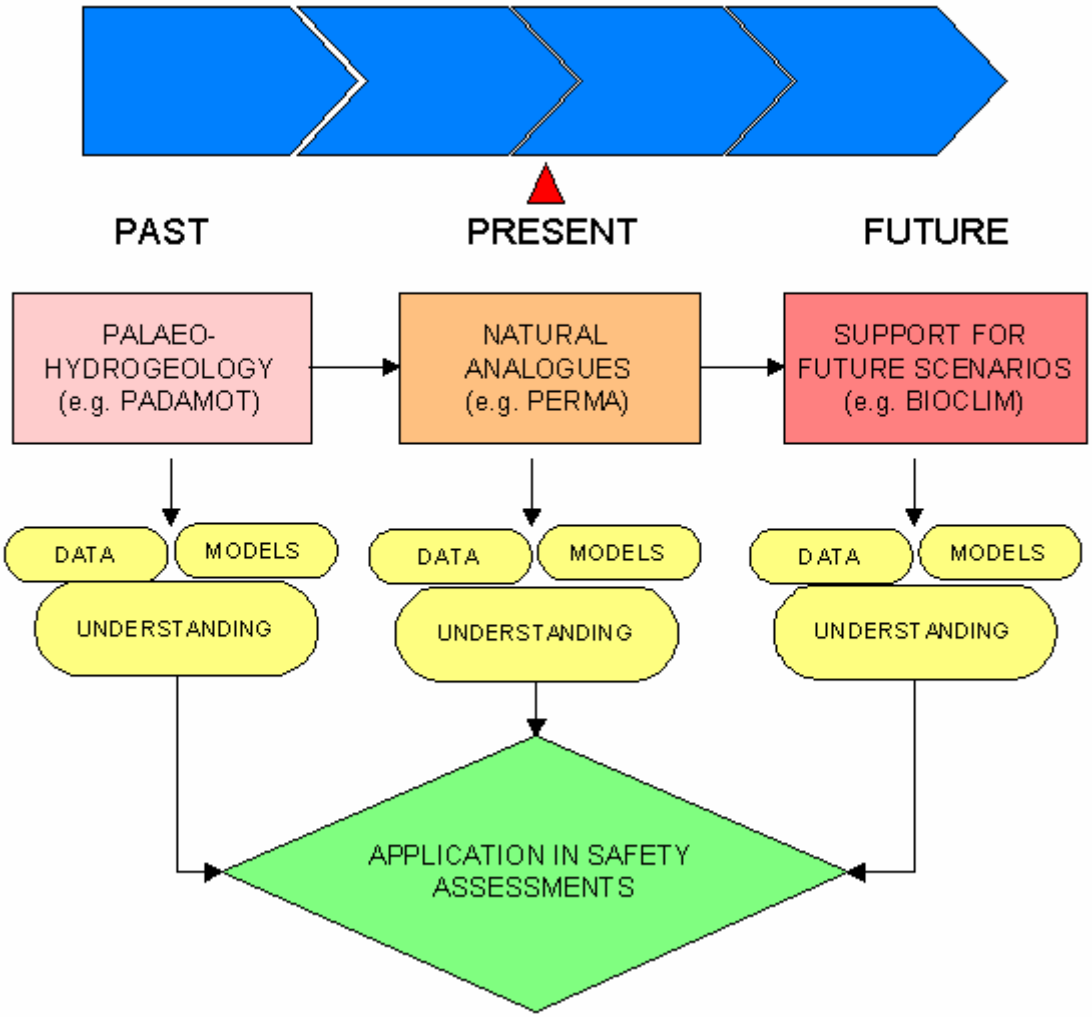


Figure 11. Palaeohydrogeology as part of a timeline of investigations to support safety assessments.

A volume of Proceedings has been produced that records the presentations, questions, answers and comments raised in discussion, as well as the group discussions (Technical Report WP1).

4 WP2: Palaeohydrogeological Analysis and Data

4.1 INTRODUCTION AND BACKGROUND

The main strategy in WP2 was to sample recently-formed secondary minerals from fractures in crystalline rock formations and to analyse these for palaeohydrogeological proxy data using mineralogical and geochemical methods. The overall scientific approach and the hypotheses that were tested, progressing from detection and characterisation of late-stage secondary minerals to interpretation in terms of past groundwater conditions and future scenarios, are illustrated in Figure 12. Calcite was the secondary mineral of principal interest in this study because of the preliminary success in the previous EQUIP study in using its mineral and geochemical characteristics to infer evidence about past groundwater conditions at study sites.

A pdf file of the report for WP2 is included on the CD-ROM at the back of this report:

> Application of Mineralogical, Petrological and Geochemical Tools for Evaluating the Palaeohydrogeological Evolution of the PADAMOT Study Sites. A.E. Milodowski, E-L. Tullborg, B. Buil, P. Gómez, M-J. Turrero, S. Haszeldine, G. England, M.R. Gillespie, T. Torres, J.E. Ortiz, J. Zachariáš, J. Silar, M. Chvátal, L. Strnad, O. Šebek, J.E. Bouch, S.R. Chenery, C. Chenery, T.J. Shepherd and J.A. McKervey. PADAMOT Project Technical Report WP2. 228 pp. January 2005.

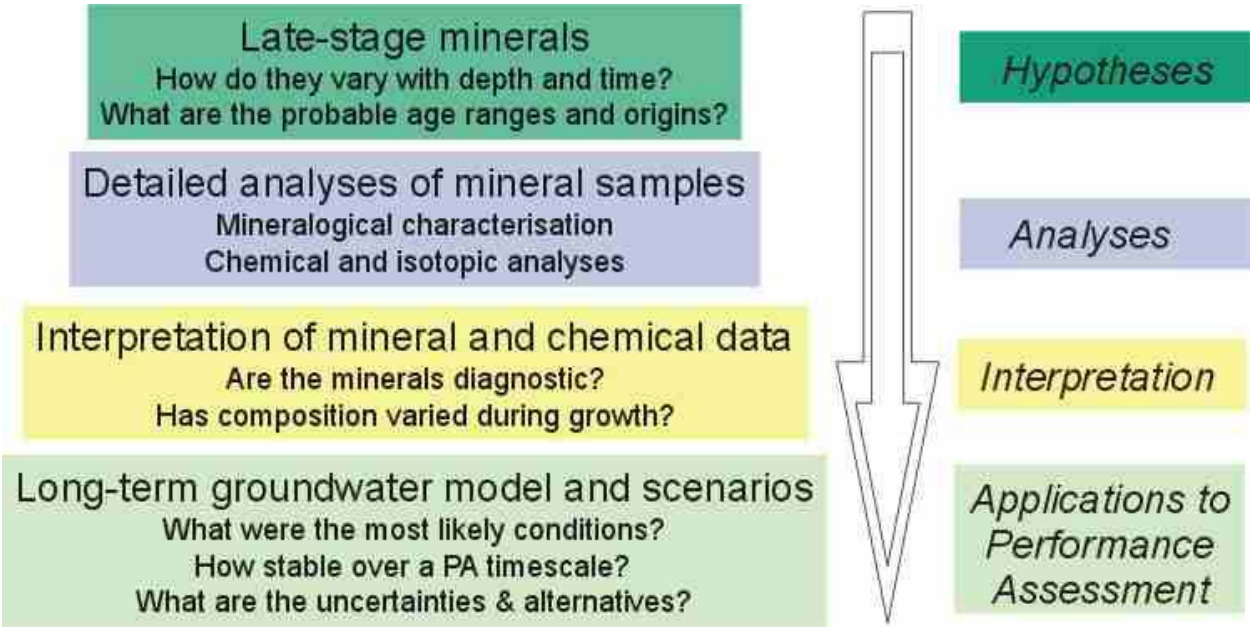


Figure 12. Schematic approach used in PADAMOT.

Earlier studies at the Sellafield site in the UK by Milodowski et al. (1997, 1998a, 2002) and research during EQUIP (Bath et al., 2000a) demonstrated that the distribution of late-stage calcite mineralization coincided closely with present-day groundwater flow paths, and could be used to identify flow zones. Furthermore, these studies indicated that the crystal morphology of calcites varied systematically with groundwater salinity. Some limited observations of the morphology of late-stage calcite from the Äspö site in Sweden were also made during EQUIP. These identified variations in crystal morphology that might reflect variations in present and/or past groundwater chemistry. Based on the experience from Sellafield, a similar study of fracture

mineralization in the Tono Granite in Japan has also indicated relationships between the morphology of late calcite mineralization and isotopic composition that suggest that saline groundwater was once present (Iwatsuki et al., 2002).

Some of the specific issues that WP2 attempted to address were:

⇒ Is the occurrence and distribution of fracture calcite sufficiently consistent and well enough understood that it could reliably be used for characterisation of some or all site types?
⇒ Under what geological, hydrogeological and climatic conditions does the growth of calcite and other minerals provide a useful record of groundwater change/stability in the recent past?
⇒ Can a transition from calcite dissolution to calcite precipitation be identified at relatively shallow depths, and how does this depend on palaeoclimate and geological conditions (both in terms of degree and rates)? Are there similar transitions for other key minerals such as pyrite and Mn/Fe oxy-hydroxides?
⇒ What are the ages of recently-formed calcites (bulk calcite and compositionally-distinct zones), and does age information with other isotopic and chemical indicators correlate reasonably with the timing and environmental impacts due to climate change during the recent past?
⇒ Are there distinctive changes in the mineral properties (zoning, morphology, etc) of calcite in different parts of the same groundwater flow path? Do these changes indicate that minerals formed in recharge areas are more sensitive to surface environmental changes than those in deep flow paths and discharge areas?

Samples were obtained from the study sites in Spain, Sweden, the UK and the Czech Republic. These locations represent different climatic zones of Europe and therefore the palaeoclimatic influences and palaeohydrogeological questions vary from site to site. The depths from which samples could be collected also varied, depending on the prior investigations carried out at each site. At some sites, samples were obtained from deep underground, from boreholes down to and beyond typical repository depths, and at other sites only near-surface samples were obtained. In the former cases, secondary calcites were investigated for evidence that groundwater conditions might have responded directly or indirectly to external influences, i.e. palaeoclimate, in the geologically-recent past. In the cases of near-surface samples, more direct interactions between palaeoclimate and groundwater conditions, hydrological and geochemical, are expected and geochemical proxies may provide information about palaeohydrology.

Among the state-of-the-art analytical techniques employed were:

- Optical petrographic analysis with transmitted and reflected light of thin sections and polished thin sections, usually after stabilising the fracture fillings materials by vacuum-impregnation with epoxy resin;
- Cold-cathode cathodoluminescence (CL) microscopy to characterize growth zoning and fabrics of secondary calcites, and also quartz mineralization (from Los Ratones only);
- Back-scattered scanning electron microscopy (BSEM) for high-resolution petrographic analyses of polished thin sections and polished blocks, secondary electron imaging (SEM) for morphological characterisation of secondary calcites, plus energy-dispersive X-ray microanalysis (EDXA) to aid mineral identification with semi-quantitative chemical analyses;
- Elemental mapping by electron microprobe (EPMA) for major and minor element compositions of secondary minerals and host rocks;
- Ion microprobe microanalysis of minor and trace elements (by secondary ion mass spectrometry SIMS), including rare earth elements, and oxygen isotopes (using a Cs primary beam) in a small set of samples from the UK sites using the facility at University of Edinburgh;

- Trace element microchemical analyses of secondary minerals and host rock minerals using laser ablation microprobe (LAMP-ICP-MS);
- Microsampling and analysis for stable O and C isotopes by helium-flushed laser-assisted carbonate extraction (He-LACE) from polished blocks or polished sections of secondary calcites;
- Conventional analyses of hand-separated bulk samples of secondary calcites for stable oxygen and carbon isotopes;
- Sr isotope analysis of hand-separated bulk samples of secondary calcites by thermal ionization mass spectrometry;
- X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) analyses for the identification of clay minerals in fracture fillings and altered wallrock samples;
- X-ray fluorescence (XRF) spectrometry and inductively-coupled plasma mass spectrometry (ICP-MS) to analyse major elements in whole rock samples, and analyses of trace elements and lead isotopes using ICP-MS;
- Microthermometric (MTA) and laser ablation (LA-ICP-MS) analyses of homogenisation/melting temperatures and chemical compositions for fluid inclusions;
- Various techniques for dating lacustrine and peat sediments, including carbon-14, U/Th isotopes, amino acid racemization and palaeomagnetism;
- Organic geochemical techniques for characterizing lacustrine and peat sediments including CHN analyses, stable carbon isotopes of organic matter, and environmental biomarkers in extracted lipids;
- Stable carbon and oxygen isotope ratios in ostracod carbonate material as palaeoclimatic and palaeohydrological proxies.

The analyses that were undertaken for each study area, the specific methodologies and the results that were obtained are described in full in the WP2 Technical Report. The main conclusions relating to present day groundwater systems and palaeohydrogeological conditions, based on the interpretations from each of the main study areas, are summarised below.

4.2 SPAIN

Site-specific studies in the granitic fractured rock of the Los Ratones Mine and the surrounding area in the southwest of Spain were aimed at providing a record of the local geofluid evolution.

Groundwaters and fracture fillings have been sampled and analysed from boreholes in the Ratones Mine at various depths to 500 m. The chemical compositions indicate that groundwaters are dilute, with Ca-Mg-HCO_3 type evolving to Na-Mg-HCO_3 and Na-HCO_3 types with depth. It is considered that ion exchange is the principal process governing dissolved cations. Most groundwaters have a δ^2H-$\delta^{18}O$ signature indicating a meteoric origin. The ^3H and ^{14}C contents indicate that residence times for most of these groundwaters vary from very short (e.g. <10 years) to 10^3 years (Ortuño et al., 1999).

The deepest waters (e.g. at 460 m) are depleted in ^2H and ^{18}O indicating an ancient origin, probably in a cold-climate period, which is consistent with residence times of around 15-16 $x10^3$ years determined by ^{14}C measurements.

Borehole core examination and detailed studies of thin sections of fracture mineralization have shown that the fracture fillings in the upper 300 m are characterized by the presence of low-temperature assemblages of iron oxyhydroxides (also with Mn) and clay minerals. Smectite is the most extensively developed clay mineral. Kaolinite is scarce, and generally occurs in fractures at a relatively shallow level (<82 m). The greater abundance of smectite relative to kaolinite is consistent with the saturation indices of the groundwaters with respect to both minerals, which indicate that most of the groundwater compositions lie in the field of smectite stability.

The saturation indices of groundwaters with respect to carbonate minerals indicate that the waters are undersaturated, consistent with the fact that neoformed calcite has not been observed petrographically. The HCO_3^- concentrations are controlled by dissolution of complex vein carbonate mineralization. Carbonate mineralization in borehole SR-3 have been differentiated on the basis of their mineralogy and chemistry into three groups of intermediate compositions in the dolomite-ankerite series. The carbonate mineralization in borehole SR-5 is more ferric in composition, comprising a sideritic end-member of the magnesite-siderite series. Both ankerite and siderite are present in borehole SR-4. Petrographical observations show that the carbonate vein minerals have suffered corrosion and dissolution to varying degrees. These minerals control the Ca, Mg, Fe and probably also Mn concentration in the groundwater.

In general, the granitic-type Na-Mg-HCO_3 and Na-HCO_3 groundwaters show a gradual decrease of Ca^{2+}, Mg^{2+} and Fe^{2+} with increasing depth and increasing distance from the Los Ratones mine. This implies that Ca, Mg and/or Fe from the dissolution of carbonates are either precipitating in new minerals or are being removed from the groundwaters by other geochemical processes. The precipitation of siderite can partially explain the excess of Ca + Mg that is found in the Ca-Mg-HCO_3 waters associated with the dolomite-ankerite vein mineralization.

Fluid inclusions in the dolomite-ankerite vein mineralization have homogenisation temperatures (T_h) of 100-160 ºC, indicating that the vein carbonates are of hydrothermal origin. This mineralization probably formed during the last major fracturing event in the area. The absence of biomarkers in the deepest calcites also supports the argument that the carbonate mineralization is geologically old. These studies have found no evidence for any young calcite or other carbonate mineralization that is currently forming in the groundwater system.

The rare earth element (REE) chemistry of groundwaters was studied as a potential geochemical tracer for water-rock interaction. In general, the waters show a moderate enrichment in HREEs relative to the granite, sometimes with a small positive Eu anomaly. Interaction with the major host granite minerals (i.e. weathering of K-feldspars, plagioclases and interactions with their aluminosilicate alteration products) alone cannot account for the REE compositions of the waters. The REE chemistry of the waters is also influenced by interactions with ankerite-dolomite mineralization (which contribute HREE), and with primary REE-rich igneous phosphate minerals (apatite, monazite, xenotime) entrained in the fracture mineralization. In addition, competing processes such as organic complex formation, the removal of REEs through the precipitation of carbonates, secondary oxyhydroxides of Fe and other metals, sorption on phyllosilicates, and the potential for colloidal transport can also be considered to influence the REE geochemistry of the mine waters.

In summary, no fracture mineralization of late-stage calcite has been identified in the hydraulically-active groundwater system at Los Ratones to the depths accessible with available borehole drillcores. Consequently, the proposed palaeohydrogeological methods based on secondary calcite studies have not been feasible.

Overall, the mineral-groundwater relationships show that the chemistry of the groundwaters in the mine are the result of interaction between the groundwaters and the granite and the fracture mineralization in the mine area. The groundwater flow system characteristic of this area involves waters with a wide range of travel times: very recent water (3 to 5 years old), modern waters of about 50 years of age, and older waters from about one thousand years to a few tens of thousands (15,000 to 16,000 years). These have produced alteration and secondary fracture filling minerals several times in the past, which have acted as sinks and sources of the elements now circulating waters in the system.

The following conceptual model of the processes related to carbonate geochemistry is proposed:

1. The oxidation and dissolution of sulphides must be taking place in the shallow zone due to the infiltration of meteoric waters rich in dissolved oxygen. This reaction releases H^+, SO_4^{2-} and Fe^{2+} to the water, as well as other metals derived from the sulphides.

2. The gradual dissolution of ankeritic carbonate fracture mineralization (also present at shallow levels) buffers the acidity produced by sulphide oxidation
3. Subsequently, the dissolved HCO_3^- reacts with Fe^{2+} and down-gradient the groundwater eventually reaches saturation with respect to siderite.

These processes were the subject of reactive transport geochemical modelling in WP4.

4.3 SWEDEN

Selection of samples from drillcore from Laxemar borehole KLX01 focussed on calcite from fractures that could be considered to be hydraulically conductive, using the following criteria (i) correspondence of fractures with borehole flow logs produced by hydraulic testing, and (ii) evidence in core of natural (in situ) open fractures. These were defined on the basis of petrographical criteria as having either intact 'gapped' pore space or being lined by euhedral calcite indicating crystal growth into open pore space.

Late-stage low temperature mineralization is dominated at depth by calcite (with some pyrite) and close to the surface by Fe-oxyhydroxide related to the percolation of oxidizing meteoric groundwater alteration (i.e. weathering). Formation of clay minerals has probably been very slow and recently-formed clay minerals exist in very small amounts (based on observations from previous studies by Bath et al., 2000a, and references therein). Present-day groundwater conditions are interpreted to be reducing and calcite-saturated below 50-100 m, based on the presence of late-stage pyrite and calcite in open hydraulically conductive fractures (Tullborg 1997).

Based on the core-scale logging of 'potential flowing features' (PFFs), 39 samples were selected from borehole KLX01 for detailed SEM studies to characterise minerals coating fracture surfaces and to refine the definition of calcite morphology. The results showed an irregular variation in late calcite crystal morphology versus depth. Calcite morphology in the upper part of KLX01 core is very variable, with alternations between c-axis flattened, equant and c-axis elongated crystal forms.

Unlike what has been found at Sellafield, Dounreay and Äspö, the late calcite in Laxemar borehole KLX01 does not show a simple change in morphology from short c-axis to long c-axis crystal forms reflecting a progressive increase in salinity with depth. The situation at Laxemar appears to be more complex: the late calcite has variable morphology in the upper 300 m, indicating local variations in palaeosalinity between different, possibly isolated, fracture flow paths. Morphology suggests a general increase in palaeosalinity from freshwater at the surface to brackish-saline water at 200 m. Below this depth the calcite morphology indicates a change back to dilute water. At depth (below 840 m), the calcite morphology has fresh water characteristics. There is some locally-preserved evidence of 'fresh water-type' calcite superseding 'saline-type' calcite, which may indicate that saline waters have been flushed or displaced by fresh water at this depth in the past.

SEM studies revealed that several of the PFFs contain coarse euhedral calcite with later very fine euhedral calcite resting on top of it. This suggests that there have been two discrete generations of late-calcite development. The earlier generation of calcite is corroded and in places separated from the later calcite by traces of smectite. This suggests that there was a discrete break between the two different stages of late calcite growth, during which the groundwater was undersaturated with respect to calcite, causing calcite dissolution, associated with very minor clay precipitation.

Cathodoluminescence (CL) petrography was carried out on a subset of 13 samples of secondary calcite from borehole KLX01 and enabled a refinement of the calcite cement stratigraphy scheme of Milodowski et al. (1998b), supported by evidence from electron microchemical maps (Figure 13).

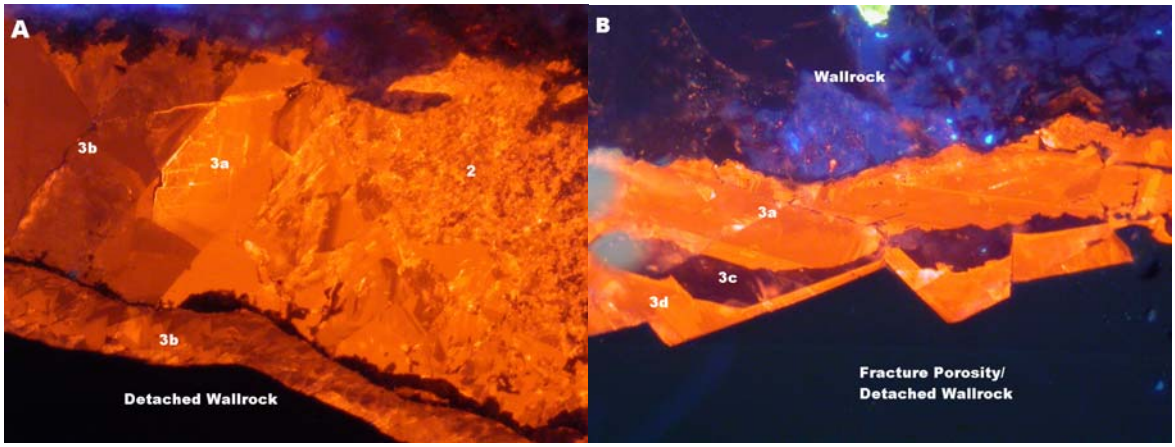


Figure 13. CL images showing the relationships between successive generations of secondary calcites, indicating episodes of calcite precipitation, overgrowth and disruption due to fracture reactivation.

Fluid inclusion studies on the same sub-set of 13 samples were limited to microthermometric analysis since no inclusions were found that were suitable for microchemical analysis. The study was limited by the difficulty in assessing whether individual inclusions are of primary or secondary origin and by the possibility that calcite with similar CL characteristics may have developed in different samples at different times.

Homogenisation temperatures of inclusions were found to be highly variable (53-195 °C), and significant proportions of monophase inclusions were also present (33 out of the 100 measured inclusions) which suggests relatively low temperatures. Salinities were also highly variable, with three components being recognised. Inclusions containing high salinity brines occurred throughout the borehole, whereas relatively fresh inclusion fluids were largely restricted to the shallower interval. In the adjacent borehole KLX02, present-day groundwaters are reported to be fresh/brackish (<600 mg/L Cl) down to approximately 1000 m depth, but below this there is a sharp transition zone with more saline groundwaters (up to 46,000 mg/L Cl; Laaksoharju et al. 1999).

The fact that high salinity fluid inclusions are found in calcite at relatively shallow depths (<255 m) suggests either that the transition zone between fresh and saline groundwater was shallower when calcite precipitated than at the present, or that the calcites are older than thought to be and are related to deep burial or hydrothermal circulation. There are a number of lines of evidence which support a young age for the calcite and therefore the first interpretation. Conversely, the high Ca:Na ratios are comparable with ratios in deep saline groundwater at Laxemar. However, the inclusion salinities are much higher than this present-day saline groundwater. It is possible that this saline groundwater is a mixture between a residual old brine from which the calcite precipitated and a dilute groundwater, that the fracture calcite has been developing over a very long time period, and that inclusion data are derived largely from the old core regions of the calcite crystals.

The selection of samples of calcite for isotopic ($\delta^{18}O$ and $\delta^{13}C$) characterization was based on the morphological characteristics of late-stage calcite. This approach, of using calcite morphology as a tool to select late-stage calcites that might have precipitated from different water types, was not possible in the earlier EQUIP studies. Where possible, calcite was sampled from the outermost fracture coating in order to analyse the most recent mineralization rather than older hydrothermal vein mineral. Analyses have been carried out on samples from borehole KSH01 from the Simpevarp peninsula, just east of the Laxemar area (Drake and Tullborg, 2004).

Euhedral late stage calcites from various boreholes in the Äspö/Simpevarp/Laxemar have $\delta^{18}O$ values ranging from -14 to -4 ‰ $_{PDB}$ and can be differentiated into three groups on the basis of their calcite morphologies:

(i) Long c-axis calcites have $\delta^{18}O$ values between -13.8 and -5.9 ‰ suggesting precipitation from different saline waters with various isotopic compositions and/or under different temperature conditions. Alternatively, there may be marked isotopic zoning within the calcite crystals.

(ii) Equant calcites have $\delta^{18}O$ values between -10.5 and -4.4 ‰, with eleven out of sixteen samples showing values in the interval -8.2 to -6.5 ‰. These isotopic compositions are consistent with precipitation from brackish Baltic Sea-type water that could have intruded during some stage in the Quaternary.

(iii) Short c-axis calcites have $\delta^{18}O$ values between -10.8 and -8.6 ‰, close to equilibrium with present groundwater (-10 ‰ $_{SMOW}$) at ambient temperature. This is consistent with precipitation from a meteoric water similar to present-day groundwater or from a somewhat cooler-climate meteoric water.

In general, the different calcite morphologies are not reflected in distinct differences in the carbon isotope composition ($\delta^{13}C$). However, short c-axis calcites have a narrower range of $\delta^{13}C$ values (-16 to -3 ‰), whereas some of the equant and long c-axis calcites have very low $\delta^{13}C$ values (<-20 ‰). $\delta^{13}C$ values in the upper 50 m have values between -15 to 0 ‰ $_{PDB}$, indicative of mixing between an atmospheric carbon contribution and biogenic CO_2 in the soil zone ('open system conditions'). At greater depth the range of $\delta^{13}C$ is larger, with both extremely positive (>+13 ‰) as well as extremely negative (<-20 ‰) values, indicative of CO_2/HCO_3 produced by microbial activity in situ ('closed system conditions'). Below 950 m depth, $\delta^{13}C$ values are between -8 and -2 ‰, indicating the absence of, or only minor contribution from, organically-modified CO_2.

Co-variation of $\delta^{13}C$ with $\delta^{18}O$ is broadly consistent with the three groups established on the basis of $\delta^{18}O$ alone: (i) 'warm brine' type calcites showing relatively large elongated crystals (mm in size), with $\delta^{18}O$ varying from -14 to -11 ‰ and $\delta^{13}C$ varying from -25 to -5 ‰; (ii) calcites with equant crystal morphology and some of the elongated crystals, with higher $\delta^{18}O$ values mostly between -8 to -6 ‰ with large variations in $\delta^{13}C$ which suggest calcite precipitation from recharged Baltic Sea water of different ages that were mixed to varying extent with meteoric waters; (iii) short c-axis nailhead calcites with a rather narrower variation in $\delta^{18}O$ and $\delta^{13}C$ consistent with precipitation from meteoric-recharged groundwater.

An attempt was made to use the He-LACE methodology to try to subsample and obtain stable isotope data from individual growth zones and generations. However, the complexity of the intergrowth of calcite of different generations proved to be on a finer scale than the current spatial resolution of the laser microsampling technique.

The different types of calcite mineralization also have a degree of co-variation of $^{87}Sr/^{86}Sr$ and $\delta^{18}O$. The oldest calcite generations show the lowest $^{87}Sr/^{86}Sr$ ratios, and the youngest calcites show the highest $^{87}Sr/^{86}Sr$ ratios (the euhedral late-stage calcite mineralization plots within this group). The few calcites with $\delta^{18}O$ values higher than -7 ‰ are found in the latter group, indicating a possible precipitation from brackish Baltic Sea water at some period during the Quaternary.

Sr, Mn and La concentrations in Laxemar-Äspö fracture calcites were determined by leaching of bulk calcite samples. Contamination was unavoidable in these very small samples because of dissolution of intergrowths and inclusions of minor aluminosilicate minerals and release of sorbed ions. Luminescence activity shown in CL analyses in these calcites has been shown to be controlled largely by Mn, with more brightly-luminescent bands corresponding to higher Mn contents (Milodowski et al., 1998b). Only occasionally does the CL variation reflect Mn:Fe ratio. Earlier studies have also indicated that Mn and La concentrations in calcite can be related

to presence of the 'organically-fed' microbial fauna, and that the concentrations decrease with depth (Pedersen et al., 1997; Tullborg et al., 1999; Bath et al., 2000a). Mn-reducing bacteria produce Mn^{2+} during the breakdown of organic material, and the Mn^{2+} is then transported in solution in groundwater and subsequently incorporated in calcite precipitates. In contrast, La is probably transported as organic and/or carbonate complexes, and is therefore likely to be less mobile when the concentrations of complexing agents (derived from the soil zone) decreases with depth.

The variations of total Mn and La concentration and of $\delta^{18}O$ in calcite from borehole KLX01 show a general pattern of higher Mn and La in calcites with $\delta^{18}O$ values in the range -11 to -7 ‰ (possibly corresponding to a meteoric or brackish sea water origin). Deep calcites from KLX01 (850 to 950 m depth) have higher Mn and La contents than deep calcites analysed in the EQUIP study (Bath et al. 2000a) which were mainly from Äspö with only a few samples from the KLX02 borehole.

Nine samples of late-stage calcite from Laxemar borehole KLX01 had sufficient material to be analysed for the presence of organic biomarker compounds. Biomarkers were found in all but two of the samples covering a depth range from the surface to over 900 m depth. Only a few organic compounds were present and in very low abundances close to the detection limits. It is considered unlikely that this is the result of contamination, since the organics were extracted from *within* the calcite only after careful acid treatment of the calcite surfaces. The compounds have survived because they have been 'encapsulated' within the calcite and protected from microbial attack. It seems most likely that the organic biomarkers, in some cases both cyclopentane and octadecanoic acid, are derived from plants. This implies that the groundwater from which these calcites precipitated contained a component that was probably recharged through the soil zone. However, microbial activity cannot be ruled out as a potential source of some of these biomarkers (e.g. in samples where octadecanoic acid only is present).

Despite the complex depth variation profile, calcite morphology together with stable isotope, strontium isotope, and trace element geochemical characteristics have helped to categorize different calcite types and generations. The use of morphology for the selection of small samples for the bulk analysis of stable isotopes and trace elements still does not overcome the problems of analysing mixed generations (since the calcite is often overgrown on earlier mineralization), nor of contamination from the presence other accessory phases. However, it does provide a possible method to help differentiate the 'end member calcites' occurring in the fractures, and, integrated with the isotopic information, the use of calcite morphology has enabled the identification of calcites precipitated from different groundwaters.

Absolute dating of the late calcite fracture fillings has so far not been possible due to very small volumes of material that can be sampled. Most of the late calcite is also either developed as thin overgrowths on old hydrothermal mineralization, or contains inclusions of older mineralization, and is very finely growth zoned with multiple generations of calcite. In addition, the U concentration of the calcites is low. This means that large bulk samples of calcite are required to provide sufficient mass of U for mass spectrometric analysis, but these samples will unavoidably contain mixed generations of mineralization.

The tentative models of the past and present groundwater circulation proposed in Bath et al. (2000a) and Tullborg (2004) are largely supported by these results. At least three zones of calcite mineralization corresponding to distinct hydrogeochemical regimes in the Laxemar-Simpevarp-Äspö groundwater system are distinguished:

- The upper part of the system is characterised by a dynamic situation involving dissolution and precipitation of new calcite. At times, biogenic activity has been significant and produced reducing conditions, whereas during other periods oxidising conditions may have prevailed. At Äspö this zone is very shallow (0-50 m approx.) but can be extended to greater depth at Laxemar (0-100 m?).

- From 100 m down to between 500-600 m mainly precipitation (or re-crystallisation) of calcite is observed. Several generations of calcite (zoned) are common at these depths. Redox conditions have probably been stable and reducing during the Quaternary, and contributions from biogenically-mediated carbonate precipitation are detected in terms of low carbon isotope values and high contents of Mn and La.
- Between 600 and 1000 m the biogenic carbonate influence decreases drastically but calcite mineralization, consistent with low temperature precipitation from fresh groundwater of meteoric origin, can be traced in the major zones of steep fractures that were intersected at 850 and 950 meters in borehole KLX01. Some of these calcites show bands with weak cathodoluminescence indicating low Mn content, but Mn-rich calcite growth bands are also found.

In contrast to the earlier studies from Äspö, it has not been possible to identify any late calcite in the Laxemar site that has precipitated from water with an isotopic composition consistent with a significant glacial component. Groundwater with a glacial meltwater component has however been identified at depths varying from 100 m (in isolated pockets) to 1100 m. One possibility is that the glacial water intrusion did not form any calcite. Alternatively, it could be that calcite precipitated from glacial-recharged groundwater simply has not yet been identified in the specific drill core samples examined to date.

At greater depth (>1000 m) recent calcite precipitation is rare, and the biogenic input seems to be insignificant due to relatively stagnant conditions that pertain at this depth in the system.

All the results (including: morphology, fluid inclusions, CL, stable C and O isotopes, and Sr isotopes) indicate that most fractures have been multiply-reactivated, and that calcite mineralization has been deposited from fluids of varying salinities and temperature regimes at different times often in the same fracture. The data also show that the position of the fresh water - saline water interface has varied considerably over time.

4.4 UNITED KINGDOM

4.4.1 Sellafield

Studies by Nirex as part of earlier site investigations and by the EQUIP project showed that the morphology of late-stage secondary calcites in the rock formations at Sellafield varies systematically with present-day groundwater composition. The present-day depth of this mineralogical transition (the Morphological Transition Zone, or MTZ) mirrors, but does not coincide exactly, with the present-day Saline Transition Zone (STZ) as defined by electrical logs. The base of the MTZ is located just above the top of the STZ. This implies that fresh water in the past was generally less deeply penetrating across the site, particularly in the centre and eastern part of the study site where the MTZ is thicker. Morphological studies of late-stage calcite indicate that there has been some movement in the position of the MTZ/STZ over time. The fabric of late-stage calcite within the MTZ predominantly indicates that younger calcite has precipitated in more dilute groundwater conditions over earlier cores of calcite which precipitated in relatively more saline conditions, indicating a progressive downward movement (between 50 to 150 m) of the MTZ/STZ during the more recent palaeohydrogeological history of the Sellafield site. Although this is the general picture of the palaeohydrogeological movement of the STZ from calcite morphologies, there is also some evidence for the position of the STZ having locally moved upwards along localised fractures/fracture zones in eastern and central parts of the site. This might reflect 'fingering' of freshwater penetration along a small number of very localised, more conductive, fracture flow paths that perhaps responded more rapidly than the bulk of the flow system to short-lived enhanced fresh water flushing events in the past.

The very limited ion microprobe study of trace halides (Cl and Br) in late-stage calcite also

suggests that palaeosalinity may have fluctuated above the MTZ but was more static below the STZ during recent palaeohydrogeological evolution of the site.

The distribution and relationships of Mn-Fe oxyhydroxide and calcite mineralization suggest that more oxidizing palaeo-waters have locally penetrated to greater depths than at present. Limited age dating of the Mn-Fe oxyhydroxide suggests that at least some of it may be late Miocene, and therefore this penetration of oxidizing alteration may represent deep Tertiary weathering following regional uplift at that time. Elsewhere however, late-stage calcite rests on, and contains inclusions of, this Mn-Fe mineralization, with 'below-MTZ type' ferromanganoan calcite (containing reduced iron and manganese) now present above these depths. The depth of development of Mn-Fe mineralization remains in the sedimentary formations but is not consistent across the study area. This possibly reflects the deeper localised penetration by fresh palaeo-groundwaters that is suggested by the MTZ, although there is no mineralogical evidence that strongly oxidizing groundwaters penetrated below the position of the current STZ.

Calcite from above the MTZ ('fresh water type') has concentric growth zones with variations mainly in the presence or absence of Mn and lower concentrations of Fe (Figure 14, top); Mg and Sr distributions also vary but are controlled largely by crystallographic sector zoning. In contrast to calcite from below the MTZ/STZ, growth zones cannot be correlated with confidence between different fractures and therefore they appear to record localised variations in the geochemical environment. The overall evolution of the zoning characteristics towards dominantly non-ferroan, non-manganoan calcite suggests that the groundwater may have become generally more oxidizing (i.e. less Fe^{2+} and Mn^{2+} in solution) with time during growth of the calcite. Ion microprobe and LAMP-ICP-MS analyses show a covariance between Fe and Mn, and an apparent general increase in concentration of both Fe and Mn with depth (Figure 15). Mn and Fe are both relatively low in the calcites from above the MTZ, and Mn varies more than Fe. Calcites from below the MTZ display a wider range of Mn and Fe concentrations with no clear depth related-trend. The fluctuations of Mn:Fe within growth zones generally decrease with depth which could indicate either generally increasing redox stability or fluctuations around an overall shift to more reducing conditions. Fe^{2+} and Mn^{2+} variations and the uncertainties in interpreting significance for palaeo-redox are considered in more detail by geochemical modelling in WP4.

Calcites from below the MTZ and STZ ('saline water type') have well-developed concentric growth zoning; up to eight distinct zones have been detected by CL which is sensitive to variations of Mn:Fe ratios (Figure 14, bottom). The high Mn:Fe calcite zones sometimes also contain inclusions of pyrite or marcasite (Bath et al., 2000a). It is suggested that the variations of Mn:Fe reflect zones of low-Fe calcite formed during discrete episodes of microbially-mediated sulphate reduction, when any Fe^{2+} in solution would preferentially have precipitated as iron sulphide, rather than significant differences in redox. EQUIP studies found that the development of the growth zone sequence in this calcite varies systematically from east to west across the site. The most complete sequence of zones is found in the boreholes from the east of the site whereas calcites from the central area show intermediate zoning and calcite from boreholes at the west of the site have a much-reduced sequence of zones. Sulphide mineralization also decreases in abundance from east to west, and is absent in the westernmost borehole. This progressive decrease in complexity of growth zoning from east to west and with increasing depth is consistent with a model whereby the flow system has evolved as meteoric invasion in the recharge area in the east, progressively displacing older groundwaters and creating new flow paths as it dissolves pre-existing anhydrite and carbonate mineralization, as it moves westward and down-gradient. The eastern (recharge) area will have experienced a longer period of meteoric invasion and porosity rejuvenation than the west of the site. Consequently, secondary calcite in the east of the site potentially records the effects of a longer history of groundwater flow and chemistry.

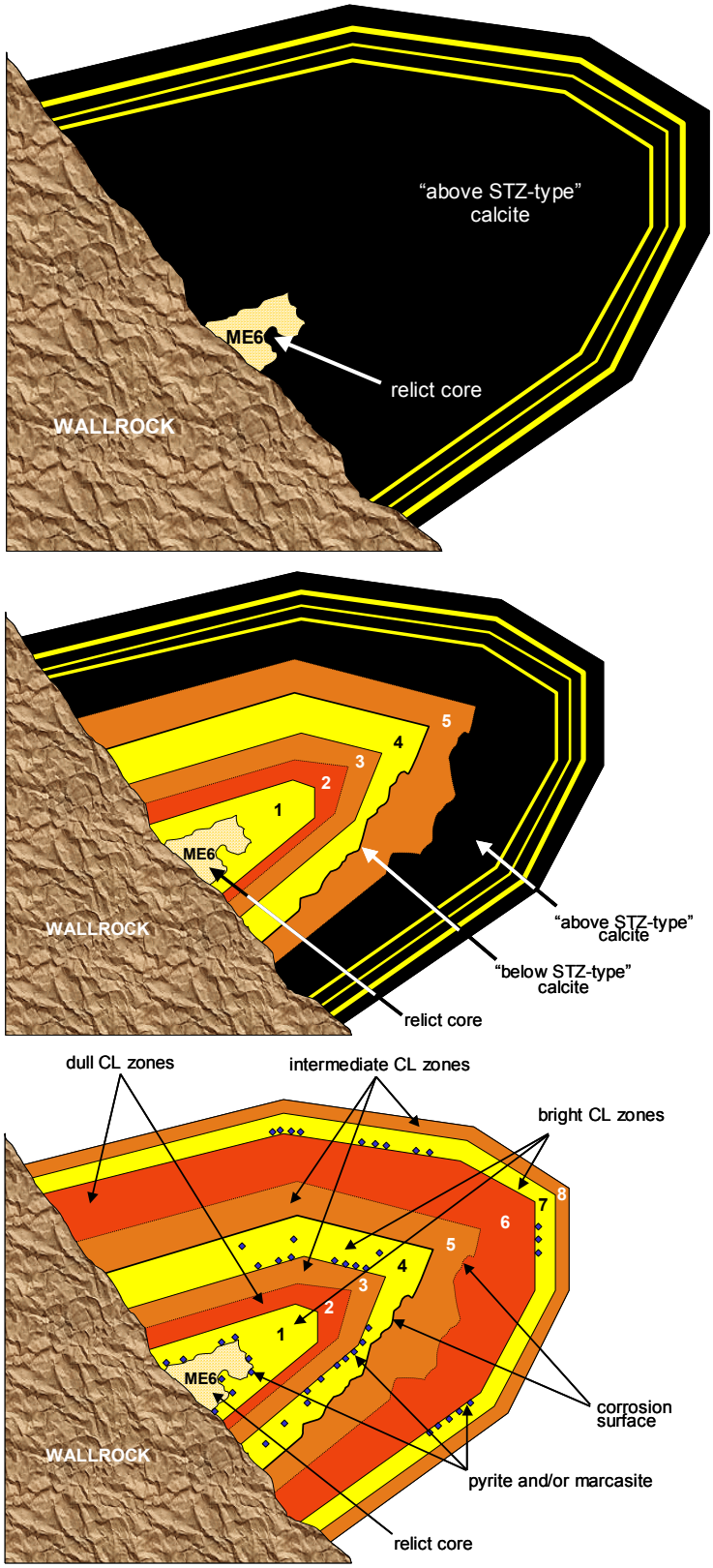


Figure 14. Schematic illustrations of CL characteristics of 'above-MTZ type' calcite from shallow fresh groundwater zone (top), calcite from the lower part of the MTZ (just above the STZ; the oldest part of the crystal is formed of calcite typical of below-STZ type and is overgrown by calcite of above-MTZ type) (middle), and of 'below-MTZ type' calcite (bottom). The numbers and distribution of bright and dark zones shown are figurative only and vary from sample to sample.

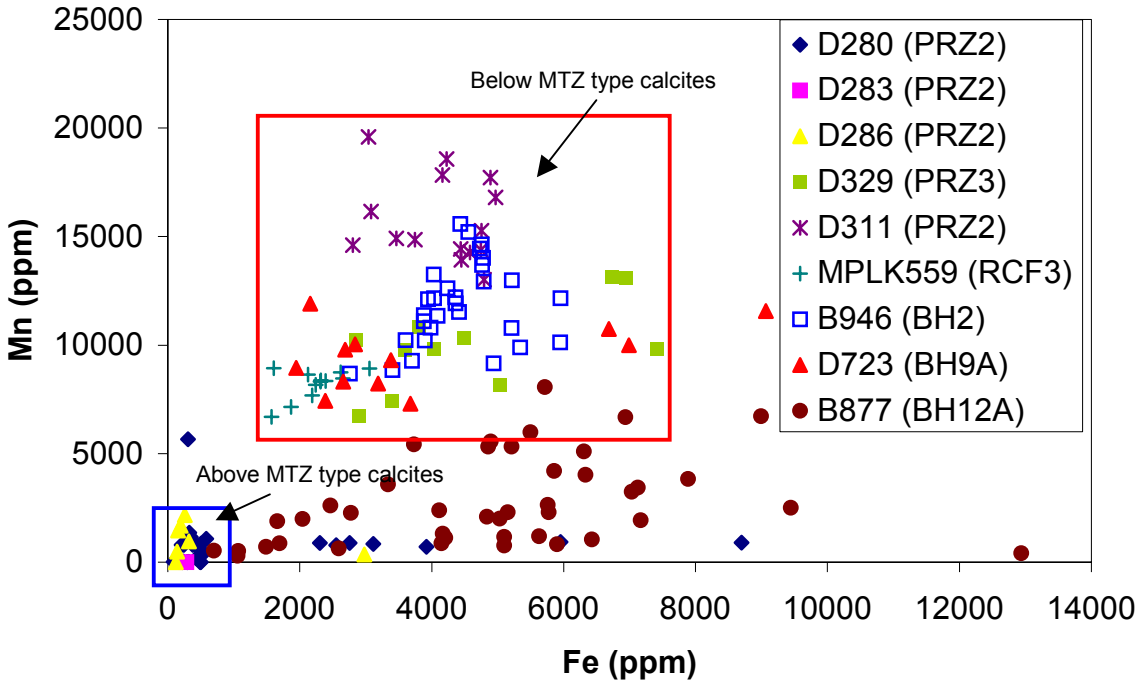


Figure 15. Analysis by LAMP-ICP-MS of Fe and Mn content in late-stage calcites from Sellafield drillcores. Blue box = field of compositions of most above-MTZ type calcites; red box = field of compositions of most below-MTZ type calcites.

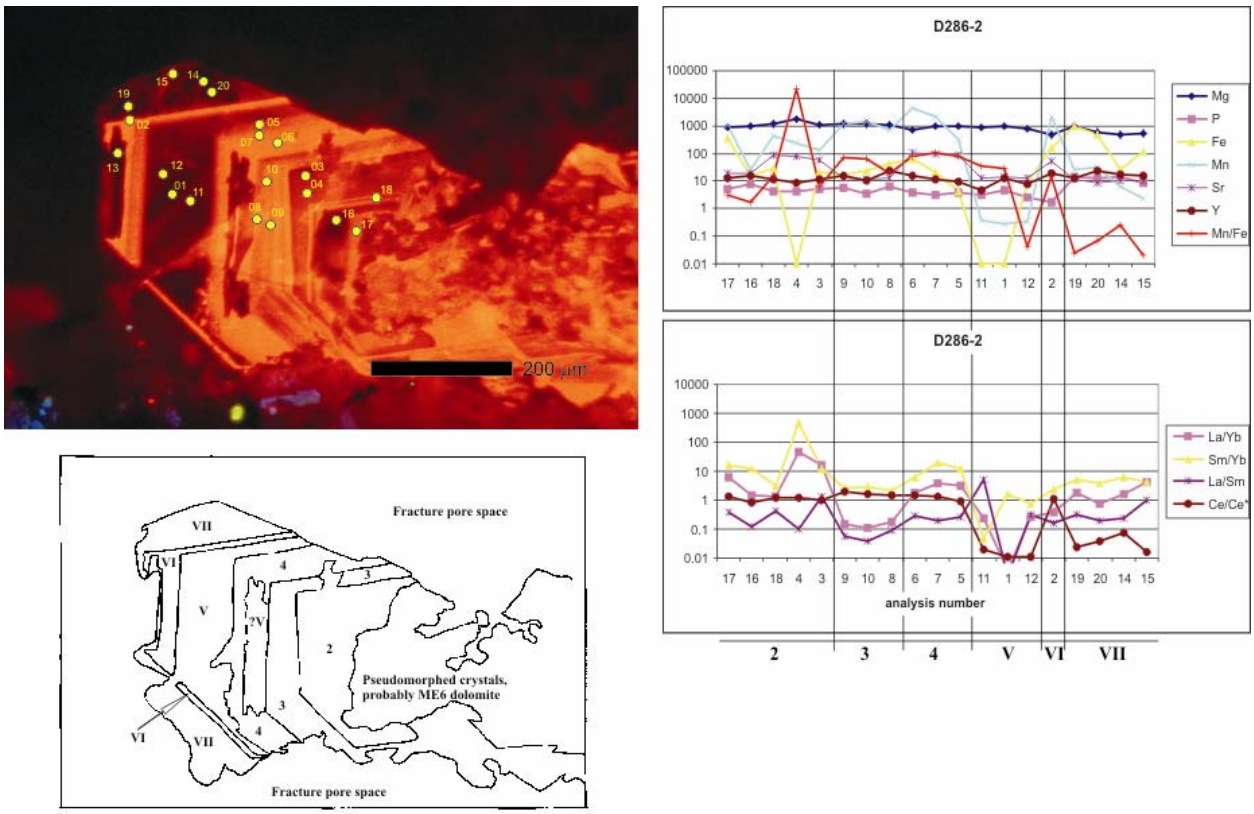


Figure 16. Cathodoluminescence characteristics, ion microprobe analysis locations, and trace element and REE compositions of above-MTZ type (shallow freshwater zone) late-stage calcite from a borehole in the centre of the Sellafield site at about 250 m depth.

Total REE concentrations (ΣREE) in calcite do not vary greatly with depth. Analyses by ion microprobe do, however, show that ΣREE varies between growth zones. Individual calcites vary internally in ΣREE from 1-2 ppm to 350 ppm. Both ion microprobe and LAMP-ICP-MS analyses show a marked difference in the distribution of the individual REEs between calcite growth zones in the shallow freshwater zone above the MTZ (Figure 16). The low-Mn, Low-Fe zones in calcite from above the MTZ also have a negative Ce anomaly (factor of 100). A similar Ce anomaly was found in a sample of manganese oxide. The Ce anomaly supports the idea that these zones precipitated from relatively oxidizing (Eh exceeding +160 mV) palaeo-groundwaters. This is the first time that a correlation of Fe:Mn variation with a Ce anomaly has been detected at a scale relating to individual growth zones within a crystal, showing the value of using ion beam or laser microsampling technology.

Fluid inclusions are very sparsely distributed in the late-stage calcite. In some cases, only one or two inclusions per wafer sample could be found. Few, if any, inclusions were observed within the youngest growth zones and these data tend to represent the early stages of mineralization and not provide information on more recent palaeohydrogeological evolution, so no fluid inclusion analyses were undertaken during PADAMOT. Analyses in EQUIP of fluid inclusions in samples from the centre of the area indicated an overall increase in salinity with depth, and that a high proportion of inclusions had salinities substantially higher (>50,000 ppm TDS) than those of the present groundwaters at the same depth (up to 25,000 ppm TDS). This indicates that more saline groundwaters were present at some stage(s) during the formation of these calcites.

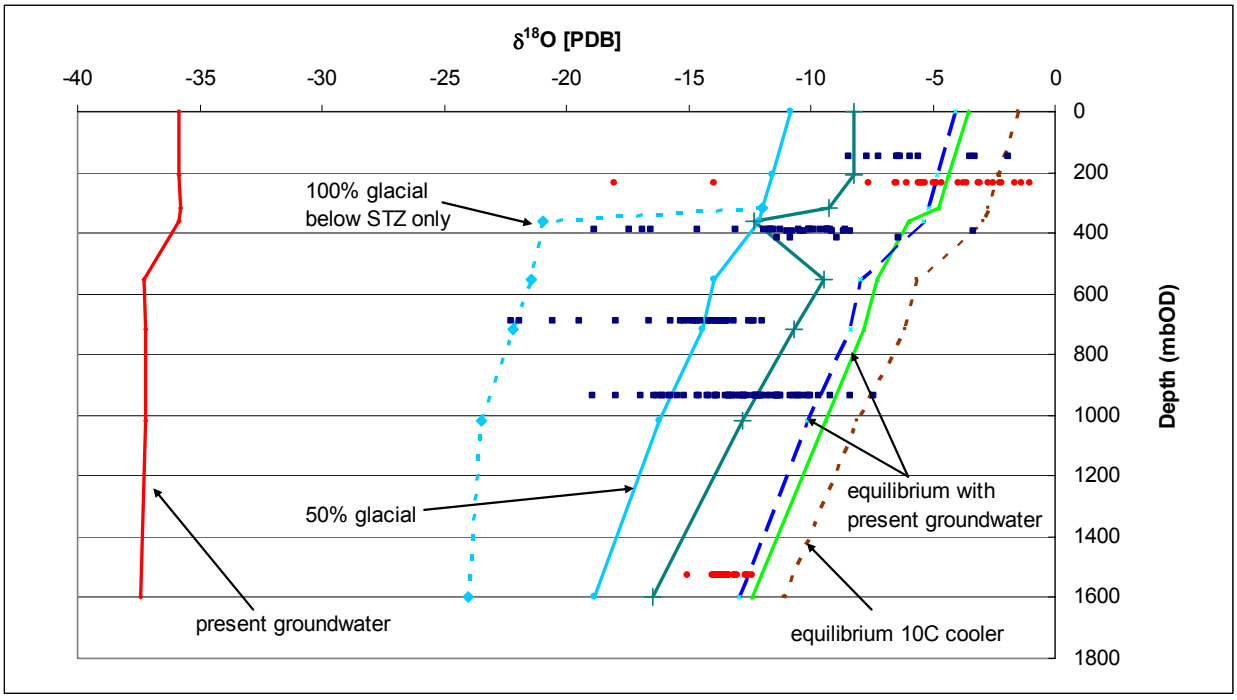


Figure 17. Oxygen isotope data for micro sampled late-stage calcites from Sellafield. Ion microprobe data are shown in red dots; He-LACE and micro drilled data are shown in dark blue dots. The present-day groundwater composition is shown by the red curve. The predicted calcite compositions in equilibrium with the present-day groundwater are shown for different $\delta^{18}O$ versus T formulae by the green and broken blue curves. Modelled calcite composition based on 10°C-cooler water is shown by the brown (broken curve). Modelled calcite compositions are also shown for glacial meltwater (assumed $\delta^{18}O_{SMOW}$ = -20‰) fractions of 50% (solid light blue) and 100% (broken light blue line for below the STZ only). The dark green central line represents the calcite composition predicted by the suggested model. Present-day water composition from Nirex (1997a).

Data for oxygen isotope ($\delta^{18}O$) microanalyses in late-stage calcite by ion microprobe and He-LACE show that many parts of calcite crystals have isotopic compositions that are significantly lighter than values calculated for equilibrium with isotopic compositions of present-day groundwaters (Figure 17). This suggests that a significant component of isotopically-light glacial water ('cold-climate water') has penetrated to depths of around 1000 m and possibly as far as 1500 m. Modelling of the $\delta^{18}O$ data suggests that glacial water could have comprised between 30 to 100% of the groundwater from which calcite grew in the fractures. The impact of potential glacial influx is strongest in the sedimentary formations and down to about 700 m, and decreases below this to about 50 % by 1000 m in the basement formation. Ion microprobe data suggest that these depleted (?glacial) $\delta^{18}O$ isotopic signatures characterize the earlier stages of calcite crystal growth. Later growth stages are less depleted, and at shallow depths above the MTZ the $\delta^{18}O$ signature of the calcite suggests growth under conditions up to 10-13 °C colder than present - possibly this could relate to the establishment of permafrost or periglacial conditions. Alternatively, the calcite composition could be explained by growth during an excursion in water sources from water with a significant glacial component, to water with a large seawater component.

It is important to note that these deeper calcites from below the MTZ/STZ with potential glacial $\delta^{18}O$ signatures are distinct from more shallow calcites, from above the MTZ, in which oxidizing palaeo-redox conditions are indicated by Ce anomalies and by Fe and Mn data, and which have heavier $\delta^{18}O$ composition. This implies that penetration by glacial meltwater cannot be correlated, on the basis of these data, with oxidizing groundwater compositions. In the case of Sellafield, observations suggest that late-stage calcite with the characteristics of oxidizing conditions in the shallow fresh groundwater system may relate to post-glacial processes.

As in the study of the late calcites from Laxemar, organic biomarkers are occasionally preserved within late-stage calcite from Sellafield. Only a small suite of samples could be examined and trace biomarkers were identified in only a few of these samples; there does not seem to be any obvious pattern to the occurrence. The data cannot be interpreted unambiguously and biomarkers could be derived from soil cover during recharge, or produced in situ by bacterial activity, or relate to the former presence of deeper basinal brines from either the hydrocarbon-bearing East Irish Sea Basin or older Carboniferous basins.

4.4.2 Dounreay

The Dounreay site was also studied, primarily because it provides an example of a coastal discharge area with upward groundwater flow, analogous to the coastal discharge area inferred to occur in the west of the Sellafield site. The mineralogical characteristics of this part of a flow system could not be studied at the Sellafield site because of the lack of cored boreholes in the near-coastal discharge area.

At Dounreay there is an overall change in morphology of the late calcite with depth, similar to that observed at Sellafield. By analogy with the Sellafield observations, the morphological studies indicate late-stage calcite at Dounreay grew from palaeo-groundwater that increased in salinity with depth. However, the position of the MTZ (about 150-370 m depth) identified from these calcite morphology observations does not coincide with the present-day STZ indicated by the fresh to brackish/saline water transition at Dounreay, the top of which starts at about 750 m depth. This implies that the MTZ at Dounreay represents the position of an older STZ, and that the STZ must have moved significantly downwards over time. This is also supported to some extent by fluid inclusion data, which show the presence of inclusion fluids which are more saline than the present groundwater; however, a high proportion of the fluid inclusion information is derived from geologically-old core zones of the calcite which may not have correspond to the time of STZ movement.

The pattern of morphological variation is not as clearly defined in late-stage calcite at Dounreay as at Sellafield. Sporadic occurrences of calcite characteristic of the freshwater zone are found

in fractures within the saline groundwater zone in the basement. The deepest sample of late-stage calcite studied in borehole NDN1 (1172 m depth) shows the development of overgrowths of fresh water-type calcite on earlier saline water-type calcite. The CL characteristics of the Dounreay late overgrowths are very similar to those seen in the 'above-MTZ type' calcite from Sellafield. This implies penetration of fresh water to considerable depth along isolated or localized fracture zones in the past. An analogous situation is concluded from observations at the Laxemar and Äspö sites.

In contrast to the Sellafield site, the late-stage calcites from the fresh water zone at Dounreay are dominantly Mn- and Mg-rich. Ion microprobe and LAMP-ICP-MS data indicate only small variations in minor and trace element chemistry during the growth of these calcites. They lack the striking zoning pattern of alternations of non-ferroan, non-manganoan calcite and manganoan calcite, and also do not have a marked Ce-depletion as seen in the 'above-MTZ type' calcite at Sellafield. This indicates that, unlike Sellafield, the fresh water zone has not been strongly oxidizing (except at very shallow levels affected by recent weathering, and associated with pyrite and ferroan carbonate dissolution and oxidation) within most of the sequence in Dounreay borehole NDN1. The apparent absence of strongly oxidising conditions in the freshwater zone at the Dounreay site may be related to effective redox buffering of the groundwater by interaction with the hydrocarbon/organic-rich and pyritic Devonian cover rocks, or to dominantly upward or lateral flow of groundwater, rather than downwards flow of oxidising meteoric water.

Late-stage calcite in the deepest sample from Dounreay, at 1172 m, has finely alternating zoning and shows similar minor and trace element chemistry (e.g. Mn:Fe, Mg, Sr) to that seen in the fresh water (above STZ-type) calcite at Sellafield except that there is no Ce anomaly. The compositional zoning points to significant fluctuations of groundwater compositions at the time of calcite growth at >1000 m depth.

The majority of fluid inclusions in late-stage calcite from Dounreay are monophase (i.e. contain a liquid phase only) and indicate relatively cool conditions during mineral precipitation. Where inclusions contain both a liquid and a vapour phase, homogenisation temperatures (T_h) are widely variable (47.5-132.5°C). Total salinities are highly variable (0.0-19.6 wt %) with a relatively high salinity component (c. >9 wt %), a moderate salinity component (c. 2-9 wt %); and a relatively fresh component (c. <2 wt %). There are no clear relationships between T_h and salinity and calcites of different generations and/or from different samples

Only limited oxygen isotope ($\delta^{18}O$) data have been obtained, using ion probe analysis and conventional analyses of micro-drilled samples. Relatively light isotopic compositions indicate that there may be a significant glacial component (30-65 % by volume) in groundwater above 500 m. If the Dounreay area was not glaciated during the Devensian (see earlier discussion), then these lighter isotopic compositions of calcites may reflect flushing by older (i.e. pre-Devensian) glacial recharge than that recorded by late calcite at Sellafield. $\delta^{18}O$ data for a deeper sample at 1172 m are isotopically heavier and are consistent with precipitation most probably from a marine groundwater source, or from a mixture of meteoric or glacial water with formation water expelled from the deep sedimentary basin (perhaps by ice loading). The Dounreay site lies on the coast and may have undergone significant isostatic depression during the Quaternary (in line with loading of the adjacent land mass at least). This would have allowed ingress of seawater immediately after glaciation and before crustal rebound.

4.4.3 Cloud Hill

Secondary calcite mineralization was studied at Cloud Hill because it was an opportunity to study calcite that had precipitated, and continues to precipitate, in the discharge area of a shallow groundwater system. This is developed as thin overgrowths on top of older calcite, which affects measurements and interpretation in several ways: (i) the morphology of the crystals is dominated by the morphology of the older substrate calcite crystals because there is often insufficient late calcite for it to display its own morphological characteristics; (ii) because of the very fine grain

size of the late calcite crystals and overgrowths, it is often extremely difficult to uniquely sub-sample the latest generation of calcite for chemical or isotopic characterization, even when using microsampling techniques such as LAMP-ICP-MS or He-LACE; (iii) it is very difficult to make observations on fluid inclusions within the late calcite because of its fine grain size and very limited presence of inclusions.

Only a few samples were analysed and the morphology of the late-stage calcite in fractures that conduct fresh groundwater at the present-day is consistent with calcite morphologies observed in the fresh water zone at Sellafield. This lends further support to the generic applicability of calcite morphology as a palaeohydrogeological indicator.

4.5 CZECH REPUBLIC

The petrological, mineralogical and geochemical characterization of fracture mineralization in the Melechov Massif is based on samples from borehole PDM-1 which was situated at the south-eastern foot of Melechov Hill. Groundwater flows were recorded at the following depths in borehole PDM-1: 17.7-18.2m; 34.6-37.0m; 50.5-51.0m; 69.0-69.5m; 73.5-74.5m; and 94.5-96.5m. The drill core from borehole PDM-1 contained very few open fractures, and minerals that had unambiguously precipitated from recent groundwater flow could not be found. Therefore, the investigations at the Melechov site focussed on a detailed geochemical and mineralogical study of low-temperature fracture fillings dominated by clay minerals (montmorillonite, nontronite, and chlorites) and Fe-Mn oxyhydroxides to provide information on the most recent rock-water interaction processes. Correlation of the studied mineral fillings with groundwater flow is suggested on indirect evidence only: (i) these low-temperature oxidative mineral assemblages are most likely to owe their origin to chemical/physical weathering; (ii) a relationship with groundwater movement can partly be inferred from the correlation of some trace element data with the present groundwater flows (indicated by hydrogeological well logging).

These fracture fillings are widely present throughout the whole sequence penetrated by the borehole and reach up to 5 mm in thickness. Even though there is no evidence about the absolute age of these fillings, these appear to be the youngest fillings encountered in the site. No carbonate mineralization was identified at this locality, either in the fractures (as groundwater precipitates) or in the host-rocks (older hydrothermal alterations).

The abundance of Fe and Mn oxyhydroxides and montmorillonite gradually increase toward the present surface. These minerals are thought to have formed as a result of low-temperature oxidative (chemical) weathering of the host granite in the shallow groundwater system. Their variation reflects the degree of weathering (i.e. weathering decreases with depth from the surface). Other neoformed clay minerals such as chlorite and illite increase in abundance with depth. Their origin is, however, ambiguous. The same mineral phases studied in the granite thin sections are clearly of hydrothermal origin.

Other minerals such as zircon, apatite, quartz, and feldspars are also found within the late-stage fracture fillings. Unlike iron and manganese oxyhydroxides and clay minerals, which are the products of chemical weathering, these minerals are resistate residual minerals derived from the host rock. It is considered that they may have been liberated from the host granite by weathering, and have been deposited in the fractures after being transported some distance in groundwater. However, it is possible that they may also in part reflect residual concentration in-situ of resistate minerals during granite weathering.

Twenty-five samples of fracture fillings, five samples of fresh granite, and one sample of paragneiss were analysed for minor and trace elements. The highest elemental contents were found for Fe (29.5 wt. %), and occasionally also Mn (5.9 wt. %) and K (5.3 wt. %). Na, Ca, Mg are present in amounts less than 1.9 wt. % each. Variations in trace element chemistry relative to the average PDM-1 granite (i.e. element enrichment/element depletion factors) are more

informative of alteration behaviour than the absolute elemental concentrations. Specific trace element data were found to be indicators of: weathering of a hydrothermal mineralization (Zn, Cu); chemical weathering of alkali feldspars (Li, Ba, Rb) and muscovite (Li, Rb); the presence of residual resistate ('detrital') phases - zircon (Zr), monazite (La, Ce, Nd, Sm).

The elemental enrichment and depletion effects are mostly strongly observed towards the surface. However, individual data are usually broadly scattered and there is often a poor correlation in this relationship. Elements such as Mg, Mn, Fe, REE, Zr, Y, U, Th, Pb, V, Ni, Co, Cu, Sr, and Be and to a lesser extent, Ca, Hf, and Rb are generally enriched towards the surface. Sr and K (and possibly Rb and Tl) tend to exhibit the opposite trend (i.e. downward enrichment); Sr shows the best correlation of the relative enrichment factor with depth. Below 100 m there is little evidence for either elemental enrichment or depletion in the major or trace element chemistry. This indicates that the recognizable depth of fracture-related weathering in the Melechov site is limited to about 100 m below the present surface.

In addition to a general trend, some elements were highly enriched at specific depths. The enrichment of Zr, REE and Y, which are typically associated with resistate heavy accessory minerals in the granite (zircon, monazite, apatite and xenotime), is interpreted to reflect concentration of these accessory minerals as they are liberated during the weathering of the parent granite. They are considered to be gravity-concentrated as a 'detrital phase' by groundwater flow, and to a limited extent they may also represent in-situ enrichment in residual weathering-resistate phases (i.e. they have not been significantly transported by groundwater).

Lead isotopes (^{208}Pb, ^{207}Pb, ^{206}Pb, ^{204}Pb) were measured on fresh rocks and fracture fillings. All the analysed samples have lead isotope ratios higher than present-day crustal lead. The fresh granite displays only a small variation of the Pb-isotope data. However, a small gradual change with depth in the Pb-isotope ratios can be observed. Fracture-fillings display a larger scatter of data than that of the fresh granite. Most of the fracture fillings form a quasi-linear trend on lead-isotope cross ratio plot. Only a few fracture fills deviate slightly from this trend. There are generally no obvious correlations between the trace and minor element chemistry and the lead isotope ratios. However, the most Pb-, U-, Zr-, REE-rich samples are usually less evolved with respect to their Pb-isotope ratios, indicating that zircon, monazite, apatite or other REE-bearing phases do not represent major causes of the observed lead isotope variations.

5 WP3: Design and Compilation of Database

The purpose of WP3 was to establish a purpose-designed database for site-specific palaeohydrogeological data and a web site for disseminating information about PADAMOT and palaeohydrogeology and for acting as a portal for project partners to access the database and the ftp server for electronic file deposition and retrieval.

A pdf file of the report for WP3 is included on the CD-ROM at the back of this report:

> Design and Compilation of Database: Final Report. T McCormick, M Nayembil and J R A Giles (Editor: P Bell). PADAMOT Project Technical Report WP3. 92 pp. November 2004.

5.1 DATABASE

The database contains primary analytical data from PADAMOT as well as from the previous palaeohydrogeological project EQUIP, plus supporting site/regional information and additional literature obtained from reviews. The central role of the database between the primary analytical and interpretative task (WP2) and the development and testing of interpretation models (WP4) is shown in Figure 18.

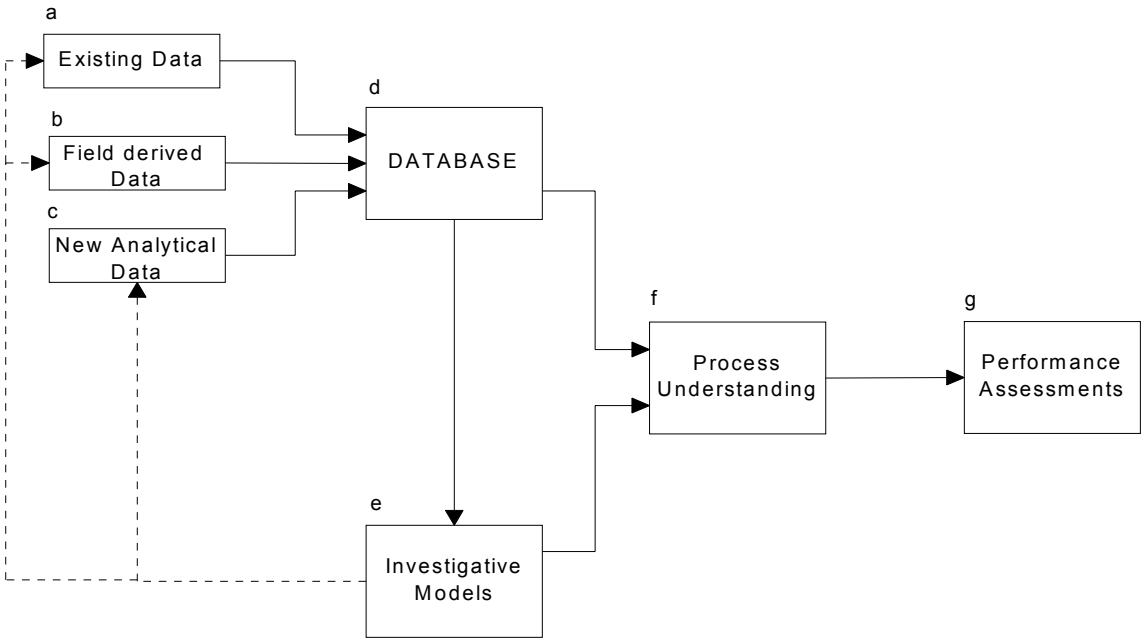


Figure 18. Schematic diagram showing the central role of the database for assembling data that can be used by process models and by PA.

The BGS designed and implemented a palaeohydrogeological database, accessible through the project web site. The various uses of the database are:

- Presentational illustration of data, information and estimated trends in palaeoclimate (and future climate) and hydrological parameters versus time;
- GIS-based 3D visualisation of distributions of samples, mineral data, hydrochemical data, etc;
- GIS-based 2D visualisation of time-variant patterns in climate features such as ice sheet growth, permafrost development, water table fluctuation, saline interface movement, etc;

- Presentational illustration of depth patterns in mineral, hydrochemical and isotopic data for single boreholes;
- Calibration and input data for interpretative models that estimate palaeohydrogeological information from mineral and geochemical data;
- Graphical or statistical comparisons between similar data sets from different regions or sites.

The PADAMOT database was designed specifically to support the project and the requirements of the partners. The database can be divided into two main components: (i) Data Model, (ii) Database Browser Application.

The data model was based on a requirement to hold data collected during the PADAMOT project and also during the previous EQUIP (Evidence from Quaternary Infills and Palaeohydrogeology) project. It aims to hold summary or interpreted data and some raw data in a logical, flexible and user-friendly format, allowing users to perform queries on the data. Example types of queries are:

- Borehole information;
- Sample information;
- Lithology;
- Microthermometry analysis - mineral paragenesis;
- Mineral assemblage;
- Chemical and isotopic analysis;
- Sample fracture information;
- Palaeoclimate and shallow surface information.

To allow easy referencing and cross-referencing of the data, unique identifiers, consistent with the data provided, have been incorporated into the design of the data model.

So that all PADAMOT partners could access data without the need for specialised software, a sophisticated but simple-to-use web-based application has been developed, which can be accessed from the web site. The database was constructed using Microsoft® SQL Server 2000 Standard Edition, installed on a Windows 2000 Server operating system. SQL Server is a relational database management system based on a relational data model, enables web access to data with or without additional programming. It also automates routines that extract, transform and load data from heterogeneous sources. It is a hierarchical browser, in which the user moves from one area of data to another by following clickable hyperlinks rather than using forms-based queries.

The principal modules within the application, once logged into the password-protected part of the web site via the 'databases' hyperlink, are:

- An application home page, where the visitor can select the PADAMOT test site from which they wish to see data;
- A 'site' module, showing general data for a selected site (including palaeoclimatic data and site-specific paragenesis) as well as the list of localities (almost always boreholes) available at that site;
- A 'locality' module, showing general data for a selected locality as well as the list of available samples from that locality;
- A 'petrographic sample' module, showing data for a selected sample, which may include a text description, paragenesis scheme, and results of any chemical analyses performed on it, as well as the list of subsamples made from it;

- A ‘petrographic subsample’ module, showing data for a selected subsample, which may include petrography, and the results of any chemical and fluid inclusion analyses performed on it;
- A ‘hydrochemical sample’ module, showing data for a selected hydrochemical sample and the results of analyses performed on it;
- An ‘image’ module, displaying a selected image together with data about it;
- A ‘fracture’ module, showing information about a selected fracture.

It was determined that browsing would normally follow a reasonably well-defined path, for example: from the application home page, selecting one site (e.g. Sellafield), selecting one locality from that site (e.g. ‘BH10A’), selecting a petrographic sample from that locality (e.g. ‘B685’), and selecting a subsample from that sample (e.g. ‘B685/AW1’).

The database can be interfaced with a GIS (e.g. ArcInfo, ArcView) for display and manipulation of spatial information.

The database was populated initially with summary data from the EQUIP project. The data were standardized and exported from Microsoft Excel spreadsheets and Microsoft Access databases into temporary tables in a SQL Server database using database tools. For PADAMOT data, Excel spreadsheet templates with defined data types, data lengths and dictionary values were provided to allow for standardization of data values at an early stage.

5.2 WEB SITE

The web site is available to the public via the World Wide Web at and most of the site can be used by anyone. The database and the FTP Server are accessible by project partners through the web site and are password-protected.

Objectives of the web site include:

- Explaining and promoting the purpose of the PADAMOT project and disseminating the project outputs;
- Providing a range of tools to facilitate communication among the PADAMOT project partners;
- Providing a framework and context for the PADAMOT database;
- Explaining and promoting palaeohydrogeology, especially in the context of its importance in supporting the understanding of long-term evolution of the geosphere for performance assessments of radioactive waste repositories.

It is available to the public via the World Wide Web at:

http://www.bgs.ac.uk/padamot/home.html

An image of the top part of the home page on the web site is shown in Figure 19. The database and the FTP Server are accessible by project partners through the web site and are password-protected.

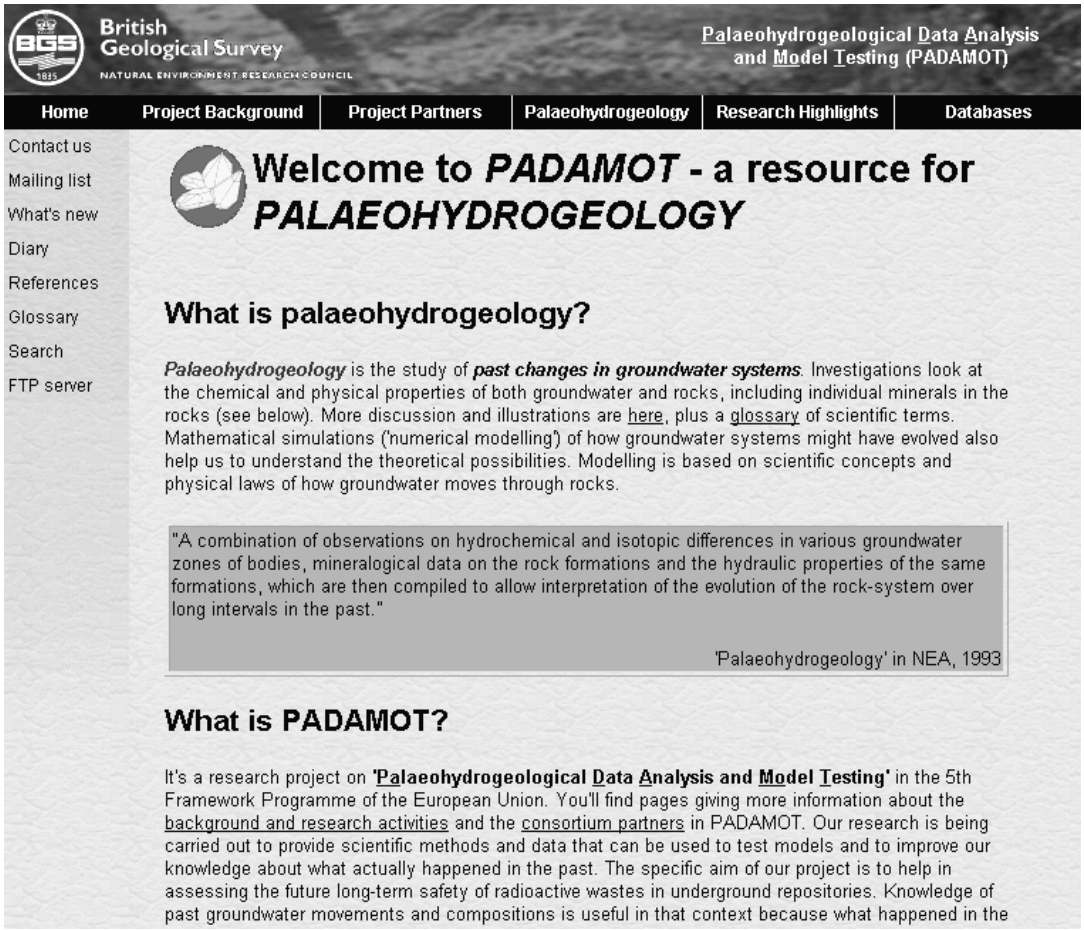


Figure 19. PADAMOT home page at http://www.bgs.ac.uk/padamot/home.html

Full details concerning the database design are provided in the Technical Report for WP3.

6 WP4: Development of Models for Process Understanding and Testing

6.1 INTRODUCTION

The objective of WP4 was to quantify palaeohydrogeological information derived from proxy data (geochemical, mineralogical, etc) by using numerical interpretative models. Four types of interpretative models have been developed with particular focus on the processes that are relevant to data that has been acquired in WP2 from the sites in Spain (Los Ratones), UK (Sellafield) and Czech Republic (Melechov).

A pdf file of the report for WP4 is included on the CD-ROM at the back of this report:

> Interpretative Modelling of Palaeohydrogeological Data: Final Report. A Bath, L Lomba, J Delgado, D Noy, B Buil, J Eugenio, V Frydrych, M Havlík, R Juncosa, J. Krásný, J Mls, M Polák, C Ruiz, T de Torres, A Cortés, F Recreo and J Šilar (Editors: A Cortés Ruiz and A Bath). PADAMOT Project Technical Report WP4. 135 pp. February 2005.

For Los Ratones, the objective was to investigate the ways that climate changes might be propagated into changes to groundwater recharge and other boundary conditions for the groundwater flow model, and thence into changes in groundwater compositions and ultimately into the geochemical and mineralogical proxies. This involved the integration of models for surface water mass balance, groundwater flow, and reactive transport of solutes. Surface water balance is an important variable for this location because of its semi-arid climate. Modelling of surface water balance was constrained by the input of information from palaeoclimatic and palaeohydrological indicators that were measured in WP2. From the analysis of palaeoclimatic indicators it was possible to derive a number of climate types which were then used to compute a water mass balance model with the VISUAL-BALAN code. Each climate type was considered representative of a given time period. Linking consecutive time periods, it was possible to obtain the time-dependent recharge function used for groundwater flow and reactive transport modelling. Groundwater flow and reactive transport were modelled together in the CORE^{2D} code to give two-dimensional distributions of groundwater compositions and of secondary mineral products, for the limiting scenarios of maximum and minimum recharge to the groundwater system.

For Sellafield, the objective was to construct a geochemical model that quantifies the processes that account for the deposition and composition of secondary calcites in fractured rock groundwater systems such as that at Sellafield. The model simulates the formation of late-stage secondary calcite due to the hydrodynamic mixing of groundwaters with different compositions in deep fractured rock systems such as at Sellafield and Äspö where variable groundwater salinities are found. Coupled flow and reactive transport modelling of hydrodynamic mixing between groundwaters with different compositions was carried out with the PRECIP and CORE^{2D} codes, showing that fluctuating flow conditions would produce growth-zoned calcite similar to that observed.

Further geochemical modelling studied the relationship between redox conditions and the Fe and Mn contents of secondary calcite. This established a quantitative theoretical basis for interpreting the significance for palaeo-redox conditions of variations of Fe and Mn in calcite growth zones. Equilibrium modelling was carried out with the PHREEQCI code (Parkhurst and Appelo, 1999) for a range of batch mixing and reaction conditions and this was supplemented by some coupled transport and reaction modelling with the PRECIP code.

For Melechov, the objective was to achieve a basic understanding of groundwater conditions in the granite massif, using numerical modelling of the spatial distribution of hydraulic potential, groundwater flows and travel times. The MENHARD code was used to construct a two-dimensional spatial model of groundwater flow. Data for calibrating the model were limited to shallow borehole tests, so hydrogeological modelling illustrates the assumptions that are necessary in extrapolating the model to deeper and longer flow paths that have palaeohydrogeological significance. These assumptions were made on the basis of analogy with other locations in the Bohemian Massif.

6.2 INTEGRATED PALAEOCLIMATE, PALAEOHYDROLOGY AND SCENARIO MODELLING - CASE STUDY: LOS RATONES

6.2.1 Reactive Transport Modelling

There are no proxy records for past climate evolution in the vicinity of Los Ratones mine, so proxy data for palaeoclimate from the sedimentary sequences of Padul and Cúllar-Baza in SE Spain were used to derive a time-dependent recharge function amenable for use at Los Ratones. This was based on computation of several models for water mass balance, taking into account the palaeoclimate interpretations of various proxy indicators: ostracods and other fossil environmental monitors, ostracod-shell stable isotope ratios ($\delta^{13}C$, $\delta^{18}O$), major and trace element composition (Mg, Ca, Sr), a large number of biomarkers and pollen content. The estimates of palaeo-recharge for Ratones were scaled relative to the interpreted data for Padul and Cúllar-Baza, according to the ratio between present-day mean annual rainfall values for the two areas.

From the analysis of palaeoclimatic indicators it was possible to derive a number of climate types which were then used to compute a mass balance for surface water with the code VISUAL-BALAN (Samper et al., 1999). Each climate type was considered representative of a given time period. Linking consecutive time periods, the time-dependent recharge functions were obtained for groundwater flow and reactive transport modelling which was carried out with the CORE^{2D} code (Samper et al., 2000). The groundwater flow model considered the mass transfers of water in the aquifer, separated into vertical (associated with surface recharge) and horizontal (due to hydraulic gradients resulting from the given boundary conditions and/or regional groundwater flows) water movements.

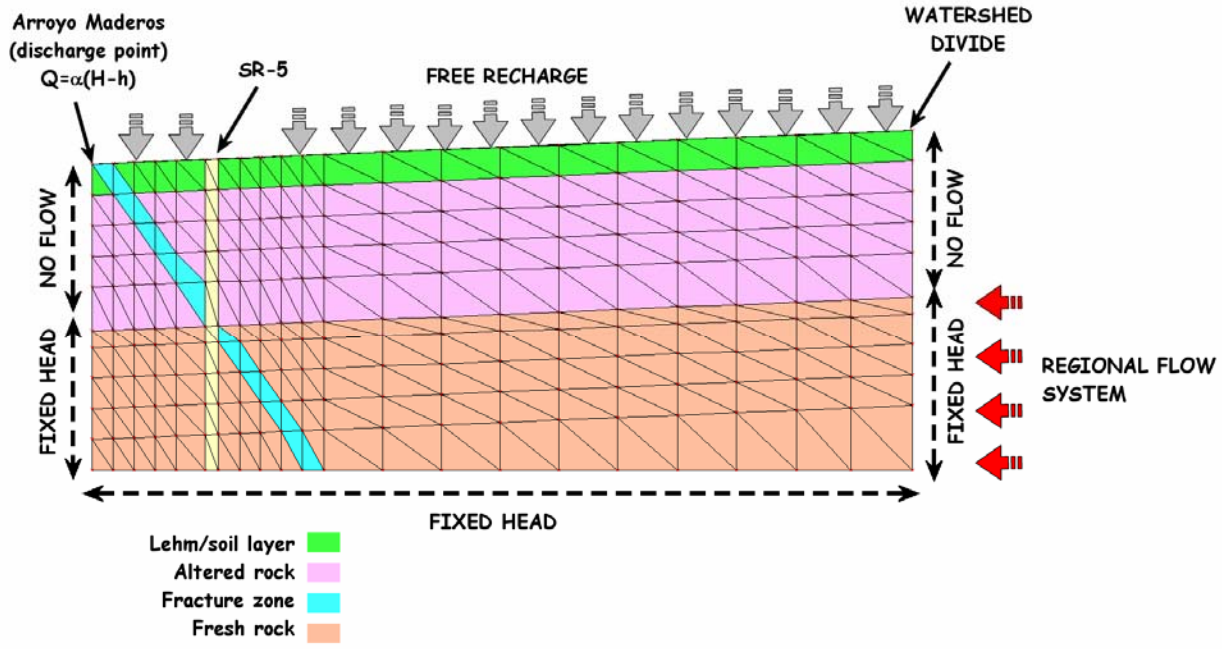
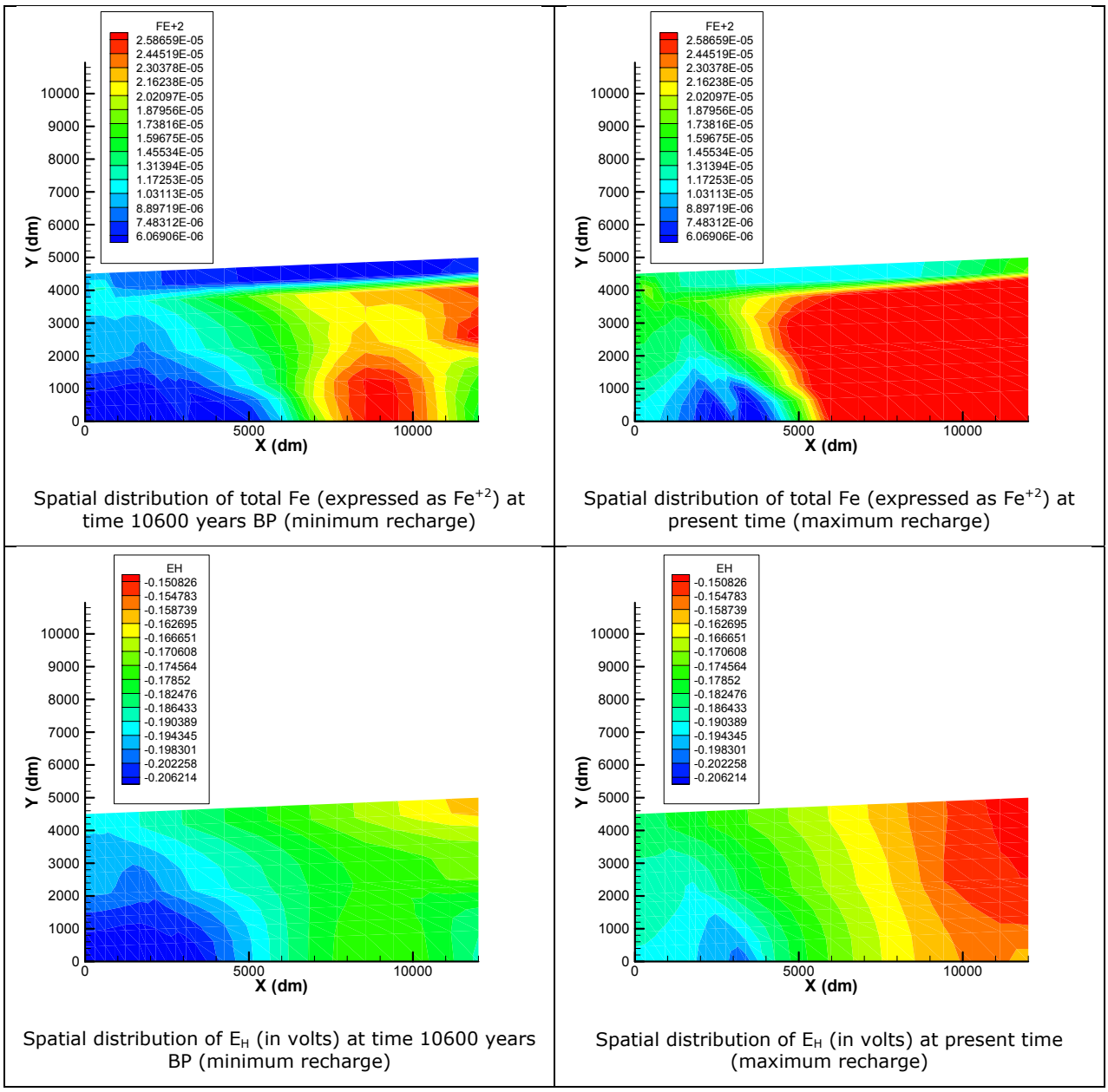


Figure 20. Finite element mesh and associated boundary conditions used in the modelling.

The reactive transport model included thirteen primary chemical components: H_2O, H^+, e^-, Na, K, Ca, Mg, Fe, Cl, HCO_3, SO_4, PO_4 and SiO_2 plus fifty-eight aqueous (secondary) species in the speciation model. The homogeneous and heterogeneous chemical reactions involved eight mineral phases: quartz, calcite, siderite, ankerite, dolomite, hydroxyapatite, goethite and pyrite. The modelling was simplified by not considering reaction kinetics except for quartz dissolution. Present-day groundwater compositions are known from extensive hydrochemical surveys. For example, significant changes are observed as a function of depth in the vicinity of the SR-5 borehole that must be related to different residence times and reactive histories of the recharge waters.



Spatial distribution of total Fe (expressed as Fe^{+2}) at time 10600 years BP (minimum recharge)

Spatial distribution of total Fe (expressed as Fe^{+2}) at present time (maximum recharge)

Spatial distribution of E_H (in volts) at time 10600 years BP (minimum recharge)

Spatial distribution of E_H (in volts) at present time (maximum recharge)

Figure 21. CORE^{2D} modelling of the spatial distribution of total dissolved iron content and redox at 10600 years (left) and present-day (right) representing minimum and maximum recharge to the Ratones groundwater system.

Reactive transport modelling of the Ratones system, represented as a two-layer unconfined saturated aquifer, with transient groundwater flows influenced by time-varying recharge fluxes was carried out for time intervals from 120 and 320 ky in the past up to the present (Figure 20).

Initial modelling simulated the transport of non-reactive ^{36}Cl and pattern of discharge to a stream downgradient of the Ratones mine. Then the evolution of the major reactive solutes was simulated, making a number of assumptions about initial water compositions and their distribution and comparing the results with present-day groundwater compositions (Figure 21).

The geochemical processes which have been invoked to account for the variable hydrochemistry found at Los Ratones system include (Gómez, 2002):

- Dissolution of carbonates (ankerite-calcite)
- Oxidation of sulfide minerals and precipitation of Fe^{3+} oxyhydroxides
- Dissolution/precipitation of apatite
- Alteration of albite to kaolinite and smectite
- Cation exchange reactions:

$$½\ Ca^{2+} + NaX \Leftrightarrow ½\ CaX_2 + Na^+$$

$$½\ Mg^{2+} + NaX \Leftrightarrow ½\ MgX_2 + Na^+$$

$$½\ Fe^{2+} + NaX \Leftrightarrow ½\ FeX_2 + Na^+$$

However in these preliminary simulations, ion exchange was omitted because there are not enough data related to ion exchange reactions (i.e. cation exchange capacities, mineral abundances, selectivity coefficients).

Sensitivity analyses tested the influence on the results of different parameters for surface water balance and groundwater flow, including parameters related to the water budget and derived recharge, permeability, porosity, leakage coefficient at the discharge point and regional flow boundary conditions. Sensitivity of the reactive transport model was also tested to various hydrodynamic and transport parameters: dispersivities (longitudinal and traverse), flow boundary conditions and diffusion coefficient.

The character and distribution of minerals suggested by forward modelling of the Ratones mine groundwater system are reasonably consistent with what has been observed in the field. Although proxy data for palaeoclimate from Padul and Cúllar-Baza were used to calibrate the time-varying pattern of recharge used in the model, the model lacked other palaeohydrogeological indicators (e.g. secondary calcite, isotope hydrology) that would provide some checks on the way that the model simulated the evolution of groundwater conditions at different points in time.

6.2.2 Outcomes and Recommendations

Future applications of this approach for performance assessment groundwater modelling would need to successfully integrate:

(a) Data and information interpreted from palaeoindicators in order to deduce how climate has evolved to the points in time being considered. This means a detailed reconstruction of *in situ* climate conditions experienced up to each point in time that is being analysed.

(b) Information recorded from meteorological stations in areas that can be used as analogues of the site and groundwater system to be modelled in which palaeoindicators constrain the evolution of conditions. The model allows palaeorecharge of the groundwater system to be quantitatively evaluated.

(c) Geological and hydrogeological properties of the site to be assessed, considering the groundwater system either as effectively at steady-state for the purpose of assessment or in a transient state, and

(d) Hydrogeochemical and mineralogical characteristics that provide palaeohydrogeological information about long-term reactive transport and hydrogeochemical evolution in the past.

This integration allows us to understand the climatic and hydrogeologic performance of the repository site in the past by constructing palaeoclimate-hydrogeochemical 'scenarios' at various time slices, taking into consideration:

- Climate conditions at each time slice,
- Hydrogeochemical and mineralogical signatures at the same time slices and at repository depth, and
- Evolutionary trends of deep hydrogeochemical conditions in relation to climate changes.

Performance Assessments for deep repositories have to project conditions into future timeframes. So the value of this approach based on 'the past as the key to the future' depends on the degree of our understanding of how future climate and hydrogeological conditions might compare with past conditions. Thus, in addition to the above mentioned methodological steps, it is necessary to take into account a further step of forecasting local and regional climate conditions during the time periods when those poorly-retarded long-lived radionuclides that could migrate from the waste repository and return to the biosphere might pose a radiological hazard.

The BIOCLIM Project has proposed a methodology to address this issue of long-term climate change, through the use of climate models and a scheme for investigating the impacts of climate and environmental change in Performance Assessment (Recreo et al., 2005).

6.3 GEOCHEMICAL MODELLING OF SECONDARY CALCITE FORMATION AND ITS COMPOSITION IN DEEP SALINE GROUNDWATERS – CASE STUDY: SELLAFIELD

6.3.1 Introduction

In the first part of this task, geochemical modelling was carried out to investigate the reactions that might account for secondary calcite to be precipitated in a deep groundwater system at Sellafield. It was hypothesised that dispersion and mixing of waters with differing compositions was responsible. Although the model was set up with data that are specific to Sellafield, the general concept of mixing between groundwaters with different salinities is typical of other sites and the model and approach have generic applicability.

In the second part of the task, geochemical modelling was carried out to investigate quantitatively the factors that control Fe and Mn concentrations in groundwaters: primarily the ambient redox conditions and the identity of the mineral phases containing Fe and Mn. The aim was to understand the significance of zoning of Fe and Mn contents in secondary calcite with respect to past redox. The approach assumed that Fe:Mn ratios in secondary calcites are the same as Fe:Mn ratios in co-existing groundwater at the time of precipitation. It was proposed that a sound basis for palaeohydrogeological interpretation of redox conditions is a dual approach of geochemical modelling of Fe and Mn, as developed here, and empirical correlation with other redox indicators in solid phases or fluid inclusions.

6.3.2 Secondary Calcite Formation

Precipitation of secondary calcite was modelled in a 1D simulation with the PRECIP code (Noy, 1998). The geometrical concept of the simulation was a 1D fracture that traverses a zone of groundwater mixing (Figure 22). Hydrochemical data representing fresh and saline groundwaters were selected as reference waters from a large data set from earlier Nirex investigations at Sellafield (Nirex, 1997a; Bath et al., 2005). One or both of the reference groundwaters flows along the fracture, with possibilities for dispersive mixing within the fracture and diffusive exchange with the adjacent matrix ('dual porosity' type of system). Some of these simulations were replicated using the CORE^{2D} code as a basis for comparing performance and capabilities of the two codes. Then CORE^{2D} was used to model repeated cycles of mixing and reaction as simulations of the development of successive growth zones in calcite. The second stage of geochemical modelling involved using PHREEQC2 and PRECIP to investigate the evolution of water compositions with respect to redox, Fe and Mn.

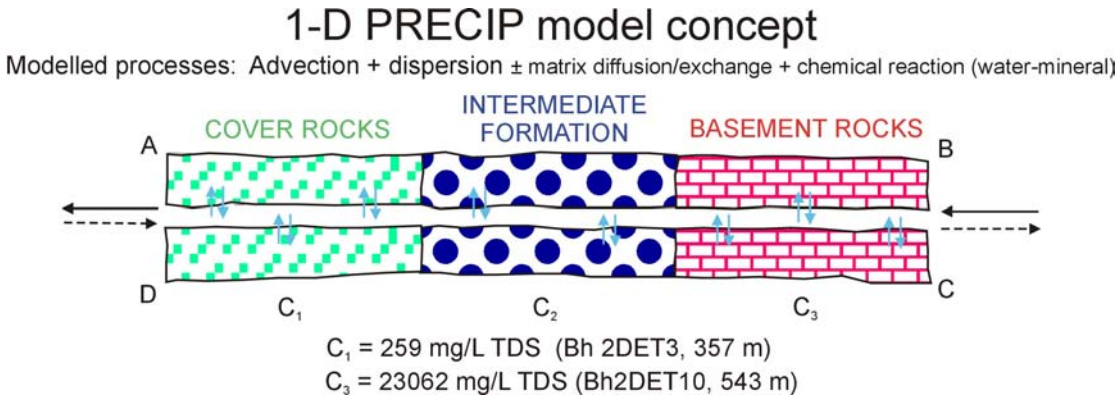


Figure 22. Processes and parameters for the PRECIP model of advection-diffusion-reaction in a fracture with an interface between fresh-brackish and saline groundwaters.

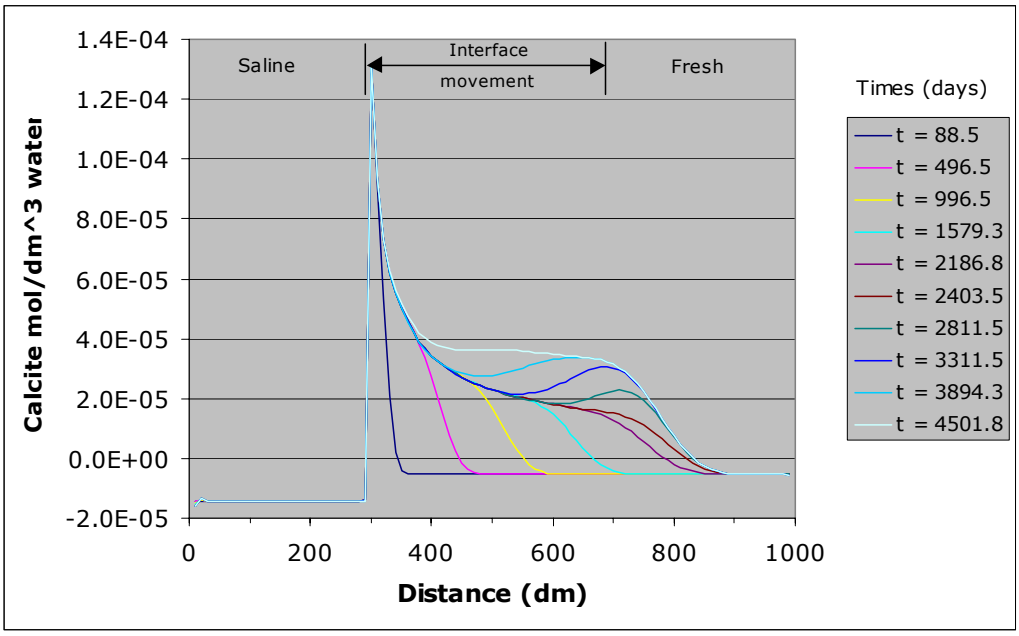


Figure 23. Amounts of precipitated calcite (in moles per litre of water) in a fracture containing fresh water (on the right) and saline water (on the left) with a sharp interface between them initially; the model simulates the position of the interface moving 400 m into the fresh water zone and then back to its original position over 12 years. Simulated with CORE^{2D} without matrix exchange.

The insights gained from the modelling of calcite precipitation are:

- The model is able to simulate the precipitation of secondary calcite as a result of advective-dispersive-diffusive mixing between fresh and saline groundwaters in porous matrices ('diagenetic cementation') and in fractures ('fracture calcite').
- Although it has not been explicitly modelled, calcite dissolution could also be simulated under certain conditions of advective-dispersive-diffusive mixing or by geochemical conditions such as rising P_{CO2} or sulphide mineral oxidation.
- The amounts and distribution of precipitated calcite in a fracture depend on whether fresh water is advancing into saline water or vice versa, and also on the degree of diffusive exchange with matrix pore water solutes.
- A possible mechanism has been confirmed for the growth of zoned calcites when a groundwater system has temporally-varying water compositions due to the hydrodynamic effects of changes at external boundaries (Figure 23).
- This growth zoning may also be a palaeohydrogeological archive of other changes in hydrochemical conditions. The next stage of modelling simulated the distribution of Fe and Mn into secondary calcite and thus illustrates a mechanism that explains variations of cathodoluminescence between growth zones.

6.3.3 Fe and Mn in Secondary Calcite as Palaeo-redox Indicator

The modelling approach used to construct geochemical models that calculate Fe and Mn concentrations in component waters and in the mixed groundwater from which secondary calcite precipitates used the same component water compositions from the Sellafield data set as were used in the first part of this task.

Prior to the model simulation of mixing, each of the component groundwaters was conditioned to calcite equilibrium and was equilibrated with Fe- and Mn- containing phases to fix the Fe and Mn concentrations. Fe concentrations in equilibrium with Fe-oxyhydroxide (Fe-ox) are insensitive to pH whereas Mn concentrations in equilibrium with $MnCO_3$ are more sensitive to pH (decreasing as pH increases). Overall, Fe/Mn increases in these conditions as pH increases, but it remains <1. Fe concentrations in equilibrium with Fe-oxyhydroxide decrease as pe increases, i.e. as redox becomes more oxidising. In these simulations, redox is dependent upon both Fe- and Mn phases with which solution is equilibrated: the general order of oxidising potential is MnO_2 > Fe-oxyhydroxide (more oxidising at lower pH) >$FeCO_3$, Fe concentrations are highest in equilibrium with $FeCO_3$, in which redox condition is reducing, and in this case Fe/Mn>1.

The interpretation and models used in the modelling of Fe and Mn distributions in secondary calcites involved various simplifications and assumptions which place constraints and caveats on the validity of this approach. The basic interpretative model assumes that secondary calcite is precipitated as a result of ongoing slow dispersive mixing of groundwaters with different compositions, e.g. typified by a fresh water and a saline water, and that these waters are already 'mature', i.e. they are at equilibrium with calcite and dissolved Fe and Mn are in equilibrium with corresponding oxide or carbonate phases or, for Fe, with pyrite. Two alternative geochemical conditions for the mixed groundwater were considered: either that secondary calcite forms without any re-equilibration of the mixed groundwater with Fe and Mn phases, or that the mixed groundwater re-equilibrates with co-existing Fe and Mn phases at the same time as precipitating calcite. In the context of the latter case, it is noted that pyrite is observed to coexist with, i.e. to have formed simultaneously with, low-Fe, high Mn:Fe growth zones in below STZ-type calcites at Sellafield. These have been interpreted as the result of Fe having been preferentially sequestered into the sulphide mineral during episodes of bacterial sulphate

reduction. A further basic premise is that Fe/Mn ratios in secondary calcites are identical (or at least very similar) to those in the source groundwaters.

The results from the modelling of Fe and Mn distributions in secondary calcite show that Fe/Mn ratios should be considered in the context of geochemical and mineralogical conditions and that the assertion that low Fe/Mn ratios correspond to oxidising conditions whilst high ratios correspond to reducing conditions may not always be correct.

Oxidising palaeo-redox conditions could be indicated by very low Fe/Mn (<0.01) or by Fe/Mn close to unity (1.0 – 1.6). The caveat on the former interpretation is that the very low ratio is preserved if the mixed groundwater re-equilibrates with available pyrite and then becomes reducing. Two caveats apply to the latter interpretation. The first is that a similar Fe/Mn ratio (i.e. ~1) can occur in reducing conditions in a mixed groundwater dominated by a component water that is equilibrated with siderite, $FeCO_3$. The second is that the same Fe/Mn ratio can arise if both saline component and mixture equilibrate with available pyrite. It is clear from these caveats that the possibility of reaction of a component water and/or the resulting mixed groundwater with co-existing pyrite or siderite is an important consideration. This requires knowledge of co-existing mineral paragenesis at a microscopic scale and the exercise of expert judgement in identifying the most likely water-mineral reactions.

Reducing palaeo-redox conditions could be indicated, in addition to those conditions described in the caveats in the previous paragraph, by moderately low Fe/Mn (0.01-0.06) or by moderately high (~6) and very high (150-300) Fe/Mn ratios. The latter two conditions, with high to very high Fe/Mn, arise in groundwaters where precursor components or the mixed water equilibrate with both pyrite and Fe-oxyhydroxide. This seems an unlikely condition in which both Fe^{II} and Fe^{III} minerals co-exist and react, but it is not impossible and may be sensible in groundwaters hosted by rocks with both pyrite and hematite in the mineral assemblage. The first condition, where low Fe/Mn corresponds with reducing conditions, applies where the mixed water has substantial proportions of both the oxidising fresh component (very low Fe) and the reducing pyrite-equilibrated saline component (Fe not so low but not high either). In such a mixture of comparable proportions, the pe of the saline component is sufficient to dominate the pe of the mixture whereas the Fe concentration is quite low.

6.3.4 Outcomes and Recommendations

The outcomes from this with respect to secondary calcite growth and the interpretation of the Fe and Mn contents as 'palaeo-redox' indicators are summarised in the following:

- It is a plausible hypothesis that secondary calcite in deep groundwater environments has formed due to mixing of groundwaters with varying compositions, typically showing up as varying salinities. Other factors that might also play a part are temperature fluctuation and re-mobilisation or pre-existing carbonate mineralisation. Geochemical models for the formation of calcite (and other secondary minerals) are non-unique and therefore precipitation and dissolution conditions each occupy wide ranges of parameter space.
- Growth of secondary calcite in distinct microscopic zones may be caused by hydrodynamic fluctuations in water movements and compositions plus the influence of matrix storage and exchange. The growth zones therefore are an archive of information about the ambient geochemical conditions when they were deposited. Geochemical modelling provides the framework in which the palaeohydrogeological significance of geochemical and isotopic data can be interpreted.
- A more rigourous theoretical basis for interpreting Fe and Mn contents of calcite, and thus also of cathodoluminescence has been established. The conceptual geochemical models are not unique and involve assumptions about the reactions, water mixing and pre-existing solid phases that control dissolved Fe and Mn, and about how Fe and Mn are distributed between calcite and water. The same approach could be used in principle to assess the significance of

other redox- and pH-sensitive trace elements (such as Ce and U), but in reality the thermodynamic base for their calcite-solution distribution is inadequately understood.

- It is an oversimplifying interpretation to assert that low Fe/Mn corresponds always to oxidising conditions and that high Fe/Mn corresponds invariably to reducing conditions. Fe/Mn ratios and cathodoluminescence activity should be considered in the context of co-existing geochemical and mineralogical conditions. Very low Fe/Mn (<0.01) is indeed typical of a mixed groundwater between oxidising component waters, but the low Fe/Mn will have been preserved if the mixed groundwater then re-equilibrates with pyrite and becomes reducing. Moderate Fe/Mn (~1) is typical of perhaps the most usual geochemical system for deep mixed reducing groundwaters in which both saline component and mixed waters have equilibrated with pyrite. A similar condition evolves if siderite instead of pyrite is the redox buffer. High or very high (~6 up to ~300) Fe/Mn ratios may be unusual because they are characteristic of reducing groundwaters in which equilibration with both Fe-oxyhydroxide and pyrite has played a prominent role.

From these outcomes, there are some recommendations for researchers and site investigations:

- It is evident from quantitative modelling as well as from qualitative conceptual models of these geochemical and mineral systems that data and interpretations have substantial uncertainties and non-uniqueness. The implications need to be considered in planning research and site investigations.
- Modelling also makes it clear that robust interpretations are made possible by integration of diverse geochemical and mineralogical data. This means that a comprehensive range of sampling and analytical techniques need to be deployed to obtain distributions and paragenesis, solid solution compositions and growth zoning at microscopic scale, stable isotopic ratios, ages, trace element contents, fluid inclusion compositions, etc for secondary minerals.
- Coupled flow-transport-reaction modelling and geochemical mass budget calculations are valuable for relating geochemical changes to possible palaeohydrogeological flow conditions.
- Conceptual geochemical models for secondary calcite in shallow and deep groundwater systems are distinct, with the former involving open-system weathering in which CO_2 and other direct impacts of climate have important roles. Deep groundwaters involve groundwater mixing and closed system evolution so that the mass budgets for C and H^+ may limit carbonates and other secondary minerals. It would be valuable in site investigations and in generic research to look more closely at the locations of these two parts of the overall groundwater system. The similarity with the biosphere-geosphere interface needs to be investigated.

The main concerns of PA teams in the context of palaeohydrogeology are with time-varying changes of the groundwater flux and flow direction, chemical environment, and other scenarios that are related to climate or other external environmental changes. The significance of modelling has to be coupled with that of the geochemical and mineralogical measurements at a particular site:

- Palaeohydrogeology provides essential support to the development of scenarios and to consideration of the range of plausible scenarios related to climate and environmental changes. Modelling of the geochemical and hydrogeological processes, especially when coupled together, indicates the potential importance of step changes and thresholds to change in chemical and hydrodynamic properties of a system that are significant to PA. Equally, the 'asymmetry' of past and future conditions has to be considered so that palaeohydrogeology does not necessarily define the limitations of scenarios.

- Scientific uncertainties and alternative conceptual models and interpretations are inherent in the application of palaeohydrogeology to supporting scenario developments for PA. Modelling provides a theoretical framework for understanding the scale of these uncertainties. This understanding is particularly important with respect to the interpretative models that are involved in converting proxy data to geochemical and hydrogeological properties of a system and relating these to climatic and environmental variations over time.

6.4 SHALLOW GROUNDWATER EVOLUTION – CASE STUDY: MELECHOV

6.4.1 Groundwater Flow Model

Groundwater Vistas modelling software was used to construct a spatial model of groundwater flow in the Melechov massif. The main objective of the groundwater flow simulation was the determination of the spatial hydraulic potential distribution, flow velocities and travel times.

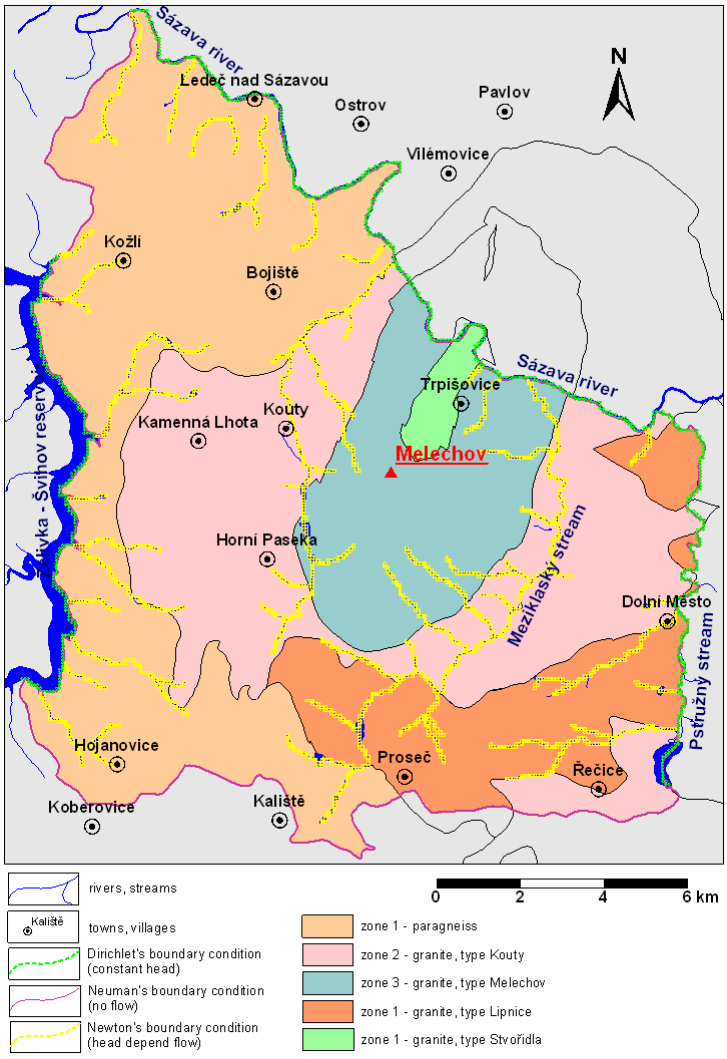


Figure 24. Model parameters and boundary condition distribution for groundwater model of Melechov area.

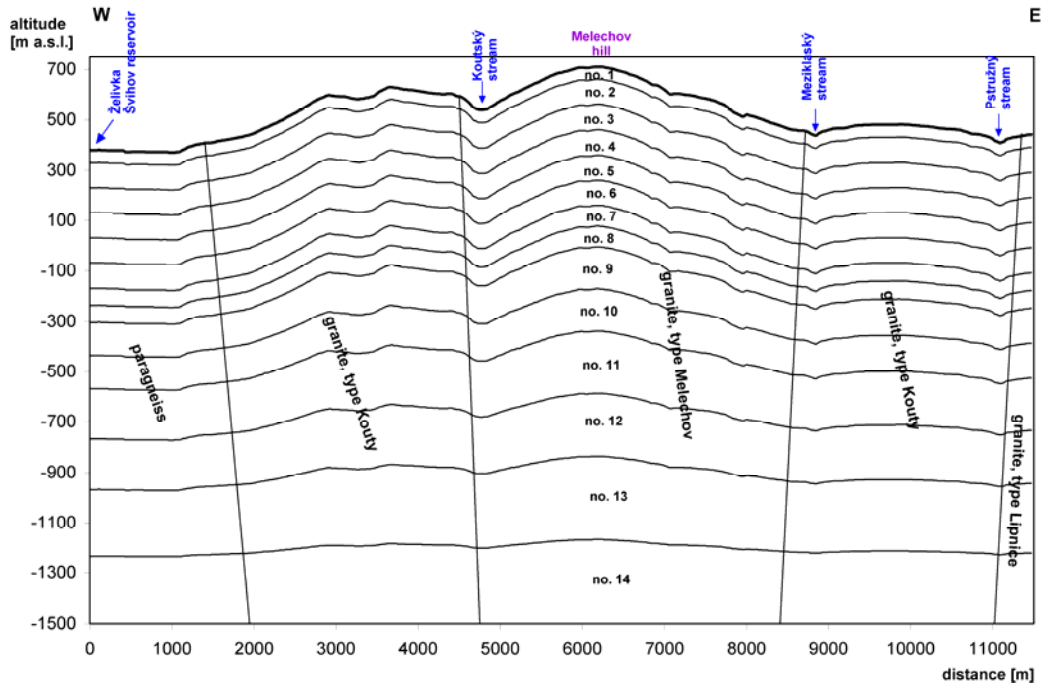


Figure 25. W-E cross-section of the Melechov massif showing groundwater model layers.

The model mesh was composed of 276 rows and 230 columns with a uniform cell length of 50 m. The total model size represents an area of 158 km^2, of which approximately 92 km^2 is actually simulated (Figure 24). In vertical cross section, the model was divided into 14 layers (Figure 25). The first layer had uniform thickness of 50 m and the next 5 layers uniform thickness of 100 m. Five hydrogeological units were identified, based on geology. These comprised the four granite types (Melechov, Kouty, Lipnice, Stvořidla) and the surrounding paragneiss. The spatial distribution of the granite types and boundary conditions is shown in Figure 24. Hydraulic conductivity was assumed to decrease with depth.

Average annual precipitation in the vicinity of the Melechov massif varies from 650 to 700 mm/year and the initial value of recharge rate was set to 4.3×10^{-9} m/s.

The main objectives of model calibration were to achieve a simulation that replicates the natural conditions in the study area. So calibration consisted of the minimization of differences between model results and known hydraulic pressure values by an initial adjustment of hydrogeological parameters. Only recharge rate and hydraulic conductivity were adjusted for model calibration. Model accuracy was compared with water table levels at selected wells and at springs with significant flow rates.

The resulting values of hydraulic conductivities in the shallow part of the Melechov massif were approximately 10x lower than values determined from pumping tests. The reason for these differences is in the thickness of the shallow model layer which is 50 m, whilst pumping tests have characterized only the part of this to depths of 30 m maximum. An initial value of recharge rate of 4.3×10^{-9} m/s was used in the model. During model calibration, this value was changed to 5.4×10^{-9} m/s. This represents 25% of the total average annual precipitation.

The model also suggests that the Sázava river and Švihov reservoir are significant groundwater discharge sinks, as are other watercourses in low-lying flat parts of the massif. The hydraulic gradient of shallow groundwater is towards the lower part of massif. With increasing depth, discharge into watercourses decreases and the topography of the regional watershed formed by the Melechov massif becomes more important.

It was necessary to assume porous medium flow to estimate flow velocities and travel times. Computations of flow velocities and travel times were performed for three cases which include

different densities of fracturing. In the model, changes in the densities of fracturing were simulated by means of changes in values for vertical hydraulic conductivity and porosity. Resulting flow velocities and travel times for various fracturing densities in the Melechov massif are shown in Table 1. The extreme values of fracturing (low and high in Table 1) represent 10-20% changes against the average values of vertical hydraulic conductivity and porosity.

Table 1. Flow velocities and travel times

depth level [m]	Average flow velocity [m·s^{-1}]			Travel time for distance of 1000 m [year]		
	low fracturing	average fracturing	high fracturing	low fracturing	average fracturing	high fracturing
0 – 100	2.40E-06	3.00E-06	3.60E-06	13	10	9
100 – 200	4.24E-07	5.30E-07	6.36E-07	75	60	50
200 – 500	5.44E-08	6.80E-08	8.16E-08	580	470	390
500 – 1000	4.64E-09	5.80E-09	6.96E-09	6800	5500	4600
1000 – 1800	3.28E-10	4.10E-10	4.92E-10	97000	77500	65000

6.4.2 Outcomes

This modelling study was the preliminary stage of developing an understanding of the present-day hydrogeology and palaeohydrogeology of the Melechov granitic massif. Calibration was severely constrained by the absence of deep boreholes and data only from the shallow borehole at Melechov. Important questions about present-day hydrogeology at the outset of modelling were:

- The effect of uncertainties in the hydrogeological properties of the deep granites on groundwater flow paths through the massif;
- The sensitivity of flow paths and travel times to infiltration;
- Travel times to discharge points in relation to depth at various points in the massif.

Palaeohydrogeology is a subsidiary objective of modelling and raises similar questions to those that concern the impact of uncertainties on the present-day groundwater model, for example:

- Changes of the groundwater flow paths and travel times at times in the past when infiltration might have been higher or lower than at present;
- Effects of changes in the properties of the upper weathered mantle on infiltration and groundwater flow at greater depths;
- Impacts of permafrost episodes when ground was partly or pervasively frozen and therefore inhibited infiltration;
- Effects of climate changes on the locations and hydrology of the boundaries of the shallow and deep groundwater systems.

Conclusions from this initial stage of modelling are summarised as:

- The depth and properties of the weathered mantle, thought to be about 30 metres deep, are important with respect to the lateral diversion of shallow groundwater which also affects the infiltration flux to deeper flow paths;
- It is necessary to investigate the relationship of hydraulic conductivity variation with the depth of the weathered mantle as identified in investigations of drillcore;

- The relationship between granite type and hydrogeological properties has been assumed for this modelling study but needs to be investigated further;
- The model has been calibrated against recharge rate by adjusting the hydraulic conductivities to obtain the best fit to the position of the water table that is known from wells and spring outflow elevations;
- Groundwater flow mainly towards the NE and W boundaries is indicated by the calibrated model, as expected from topographic considerations, but the magnitudes and directions of groundwater fluxes in the deep model layers have large uncertainties due to the assumptions about depth-dependence of hydraulic properties and about infiltration below the weathered mantle;
- Travel times and flow velocities have been calculated on the basis of the porous medium model and are, for example, in the order of 5000 years per 1000 metres flow path in the depth interval between 500-1000 m, assuming a porosity value corresponding to 'average' fracturing, but these estimates are strongly dependent on many factors including the porosity and hydraulic gradient/direction at that depth.

For making recommendations for preliminary PA scoping, the basic understanding of this system has to be developed further by additional modelling, calibration with borehole data and by comparison with other studied granites. Palaeohydrogeology needs to be developed further by establishing a series of past hydrological regimes based on known climate history, and then developing conceptual models for the palaeohydrogeological conditions that might have been associated with those regimes. An important constraint on palaeohydrogeology is the topography of the massif and the influence this has on the boundary conditions.

6.5 SUMMARY AND IMPLICATIONS FOR PALAEOHYDROGEOLOGICAL INTERPRETATIONS OF GEOCHEMICAL DATA

6.5.1 Integrating Palaeohydrogeological Data with PA Issues

WP4 had the objective of developing and applying interpretative models that are tools for: (a) understanding the processes that link the geochemical measurements made in WP2 and databased in WP3 with the evolution of past groundwater conditions, and (b) estimating parameters that are required for PA groundwater models, such as limits on boundary conditions, travel times, redox and salinity fluctuations.

Essentially, the interpretative models for process-understanding should be able to be calibrated using palaeohydrological information and provide an interface between a database of palaeohydrogeological information and FEPs for scenario development in PA.

Proxy geochemical and mineralogical data have to be interpreted using expert judgement and quantitative modelling to extract information that is relevant to FEPs and PA. The ways that these interpretations are carried out, and the extent and significance of uncertainties, are not easily apparent to PA groups. Consequently, palaeohydrogeological information has tended to be discounted when FEPs are being screened for the development of scenarios in PA. The methods developed here should help PA groups to identify and screen scenarios and to constrain them with quantitative information, for example with respect to:

- Recharge to the groundwater system in relation to future changing climate conditions,
- Hydrogeochemical behaviour and reactive transport at repository depth, for example with respect to salinity and stability of redox conditions,
- Locations and fluxes of groundwater discharge from the geosphere to the biosphere.

To meet the objectives of WP4, interpretative tools were developed to quantify interpretations or proxies as much as possible. The interpretative models also helped to clarify the uncertainties. An important part of the methodology in WP4 was the use of coupled models to examine spatial and temporal variability of processes that control palaeohydrogeological proxies. The two coupled reactive transport models that were used, CORE^{2D} and PRECIP, simulate geochemical changes coupled with groundwater flow in 2- and 1-dimensions respectively. They were used to investigate the variations of geochemical parameters and the processes underlying the interpretation of proxies so that proxy data can be used to calibrate models which could then be applied to the evolution of a site for future changing climate conditions.

Another aspect of the methodology was aimed at developing a way of interfacing different climatic and hydrological proxies with a palaeohydrogeological model as support for the construction and calibration of a groundwater model with boundary conditions appropriate for future changing climate. This was achieved in the model for Los Ratones by using the VISUAL-BALAN code to estimate time-dependent changes of recharge rate. These estimations were constrained by palaeoclimate information from measurements of microfaunal, pollen, isotopic and organic geochemical proxies in WP2. In general, the integration of models in this way should make the conceptual assumptions and uncertainties more explicit and the range of plausible palaeohydrogeological conditions better understood.

The modelling approach to understanding the hydrodynamics of the Melechov site is the initial stage in the development of a site investigation methodology that is appropriate for fractured granitic rocks in the terrain and climate of the Bohemian massif. The type of palaeohydrogeological information that will inform FEPs for this area are the proxies that contain evidence of climatic influences on recharge rate, distribution of flow between shallow and deep flow paths, and the locations of discharge at the peripheral hydrological boundaries and at intermediate topographic features. Future investigations would integrate further hydrogeological modelling for varying boundary conditions and additional geochemical studies of the palaeohydrogeological proxies that have been developed in WP2. Experience at Melechov suggested that those proxies will only be applicable at greater depth than so far investigated.

The last part of the methodology developed in WP4 involved forward modelling of geochemical proxies for redox during growth of secondary calcite. It was carried out to provide a firm basis for interpreting palaeoredox proxies measured in WP2. In this case, the conceptual assumptions regarding the groundwater mixing process and the mineral controls on Fe and Mn concentrations in solutions were made fully explicit in the model. This quantified the uncertainties in relating the geochemical proxies to redox and also described the science that underpins expert judgement.

6.5.2 Numerical Tools

WP4 deployed a range of computer codes as tools for calculating various physical and chemical conditions of the groundwater systems of interest. Notable success was demonstrated in the integration of groundwater flow, solute transport and geochemical simulations with CORE^{2D} and PRECIP.

An integration of hydrological calculations and palaeoclimate data for the upper boundary conditions of groundwaters in semi-arid conditions was demonstrated with VISUAL-BALAN. The more widely-available generic codes MODFLOW and PHREEQC, for groundwater flow and geochemical reaction respectively, were shown to be valuable for calculating ‘snapshots’ of the groundwater and geochemical properties of a system to test outcomes for particular assumptions of relevant properties, boundary conditions and other constraints.

The value of further developments and integration of numerical tools is, arguably, limited by the acquisition of palaeohydrogeological proxies that can test spatial and temporal variability with

increasing resolution and reliability. The capabilities of CORE^{2D} and PRECIP to simulate transient systems (in 2D and 1D respectively) were demonstrated in WP4, but the validity of their simulations is limited by calibration data.

Some interesting developments in palaeohydrogeological modelling are happening outside PADAMOT, most notably in SKB's site investigation project in Sweden. The 3D groundwater flow and solute transport codes CONNECTFLOW and DarcyTools have been used to simulate the evolution of groundwater chemical and isotopic compositions up to the present-day, testing assumed hydrogeological properties and initial/boundary conditions (Hartley et al., 2004; Follin et al., 2004). Geochemical reactions and equilibria are not included in these models, so essentially salinity and stable isotope composition are simulated and are the principal calibrations.

Modelling in WP4 made progress towards the integration of independent models of biosphere/climate, groundwater and geochemistry. Palaeoclimate, geochemical, isotopic and mineralogical proxies were used to calibrate the models. Integration was achieved by identifying what information needs to be transferred between the various models, e.g. recharge data from the biosphere model to the groundwater model, water flux data from the groundwater model to the geochemical model. Acquisition of proxy information, interpretation by expert judgement and modelling and understanding of uncertainties especially with respect to temporal variability are then the focus of integration between the different workgroups.

Integration will also be facilitated by having realistic modelling ambitions that recognise the differing spatial and temporal resolutions. Biosphere modelling with respect to palaeoclimate has much greater temporal resolution than is appropriate for temporal changes of boundary conditions for groundwater models. Spatial resolution in groundwater flow and solute transport models is, currently, more refined than that in transport and reaction modelling.

The possibilities and realities of integration with PA groups, especially with regard to the identification and quantification of FEPs and scenarios, is considered in the report for WP5.

7 WP5: Dissemination and Use of Results for PA

7.1 INTRODUCTION

The objectives of WP5 were: (i) to develop a methodology for incorporating palaeohydrogeological information in Performance Assessment (PA) to demonstrate safety against long-term climate scenarios; (ii) to synthesise the outputs from PADAMOT, principally those from WP2 and WP4; and (iii) to evaluate the output from PADAMOT in terms of use for PA and to communicate these results and recommendations in a way that is usable by the PA teams.

In support of these objectives, reviews undertaken in WP1 were extended in WP5. These showed that palaeohydrogeological information has been fairly widely used to support, directly and indirectly, conceptual models for site evolution in base/central scenarios or in variant scenarios in past PA exercises. In many PAs, theory-based concepts for scenario evolution have been supported qualitatively by palaeohydrogeology. The general aim of WP5 in PADAMOT was to strengthen the ways that evidence-based palaeohydrogeology is used to test and quantify the evolution scenarios being used in PA.

A pdf file of the report for WP5 is included on the CD-ROM at the back of this report:

> Dissemination and Use of Palaeohydrogeological Results for Safety Assessment. A Bath and P Degnan (Editor: A Bath). PADAMOT Project Technical Report WP5. 82 pp. January 2005

7.2 PALAEOHYDROGEOLOGY IN PAST PA EXERCISES

Performance assessments (PAs) up to the present time have generally simulated the long-term behaviour of a repository with numerical models that are parameterised for present-day conditions and that have assumed invariant conditions. The potential impacts on safety of environmental changes have been considered, if at all, by constructing alternative or variant scenarios representing possible future evolution. Alternatively, sensitivity calculations have been used to demonstrate that potential impacts of environmental changes lie within the range of uncertainty in the central or base scenario. Confidence in the validity of variant scenarios or sensitivity analyses, and in the implied overall stability of the deep geological environment, depends on independent evidence. Palaeohydrogeology and natural analogues are the two principal avenues of investigation for this type of evidence.

The climate-related scenario that is generally considered to have the greatest potential impact for those sites at northern latitudes is glaciation. Theory-based concepts of how groundwater conditions change under ice sheets and permafrost and how their potential impacts should be represented in base scenarios or variant scenarios have quite large uncertainties. These are areas where additional palaeohydrogeological information would improve the basis on which scenarios are developed for northern and central European regions that will experience glacial and/or periglacial conditions in the future.

Palaeohydrogeological evidence of the past impact of glaciation has been investigated most intensively by the programmes in Sweden, Finland, UK, Switzerland and Canada. Periglacial impacts (permafrost, meltwater run-off) have also been considered by the UK, Swedish, Finnish, Belgian and French programmes. In regions that are not susceptible to glaciation, the climatic and hydrological changes that are associated with global cycles of glacial and interglacial periods must still be considered in PA. This has been the case in Spanish and US programmes for which present-day regional climate conditions are semi-arid to arid.

Although climate-related changes in groundwater systems have been the focus of the PADAMOT project, other environmental or geological changes may also be of potential concern as variant scenarios over the timescale of PA. Palaeohydrogeological methods are equally applicable for obtaining evidence of past changes that will help to define and constrain scenarios in these cases. For example, uplift or subsidence due to plate tectonic processes is a significant, and perhaps dominant, cause of changes in the geosphere environment during a PA timescale for potential repository sites in Japan. In this case, a deep repository location does not necessarily have the simple benefit of stability that it has with respect to climatic impacts on groundwater, and thus methods for investigating palaeohydrogeology and past stability have great potential significance. Another case is the proposed repository at Yucca Mountain in the USA where the possibility of future hydrothermal activity within the PA timescale has been scrutinised closely by means of the palaeohydrogeological evidence for the existence, timing and intensity of past hydrothermal activity.

It is apparent from a review of twelve published site-specific or generic PAs that palaeohydrogeology has been used variably in past PA exercises, from being virtually absent to having a major part in supporting models for both present-day conditions and impacts of past climatic episodes (ANDRA, 2001; ENRESA, 1997, 1998, 1999; JNC, 1999, NAGRA, 1993, 2002a,b; Nirex, 1997b; ONDRAF/NIRAS, 2001; SKB, 1999; SKI, 1996; USDOE, 2000; Vieno and Nordman, 1999). To some extent this is due to the preliminary nature of many PAs carried out to date, in which the emphasis has been on evaluating safety for groundwater pathways as they are at present. Where variant groundwaters scenarios have been developed, the scope and impact of these on PA has been estimated and constrained usually by expert judgement. Evidence from site investigation to support or test such judgements has largely not yet been integrated into scenario development. In other words, the integration of site investigation data and modelling that underlies the base case for PA has not yet been extended to palaeohydrogeology and scenarios. As a result, uncertainties in scenarios might be unnecessarily high or unrealistically low.

7.3 PALAEOHYDROGEOLOGY AND FEPS

It is evident from the review that there are several different reasons why palaeohydrogeology has been used so variably and mostly patchily in PA. Amongst these reasons are:

- Focus of preliminary PA is on steady-state modelling of the system as observed; scenarios are generally little developed, absent or consider only non-geosphere features, events and processes (FEPs).
- Scenarios have been developed for ‘worst case’ conditions based on theoretical FEPs rather than realistic FEPs based on interpretations of site-specific information.
- Many PA models have been parameterised primarily with stochastic distributions of site-specific data or generic data, so that the general approach to PA modelling does not readily accommodate deterministic or interpreted palaeohydrogeological information with poorly constrained uncertainties.
- Palaeohydrogeological information, which contains variable and sometimes high degrees of uncertainty, is not expressed quantitatively as parameters that PA models can use.
- Palaeohydrogeology has mainly been considered in detail in the interpretation of site investigation data and is available in research reports as narratives.

New developments in simulation codes and greater computing power are allowing PA calculations to take account of varying ‘time-dependent’ boundary conditions and system properties (as schematised in Figure 2). However the scope for sensitivity analyses is still limited by computing power especially considering the additional number of parameters for

which sensitivity should be analysed in a time-dependent PA. Palaeohydrogeological information will be important in achieving a balance between practicality and realism.

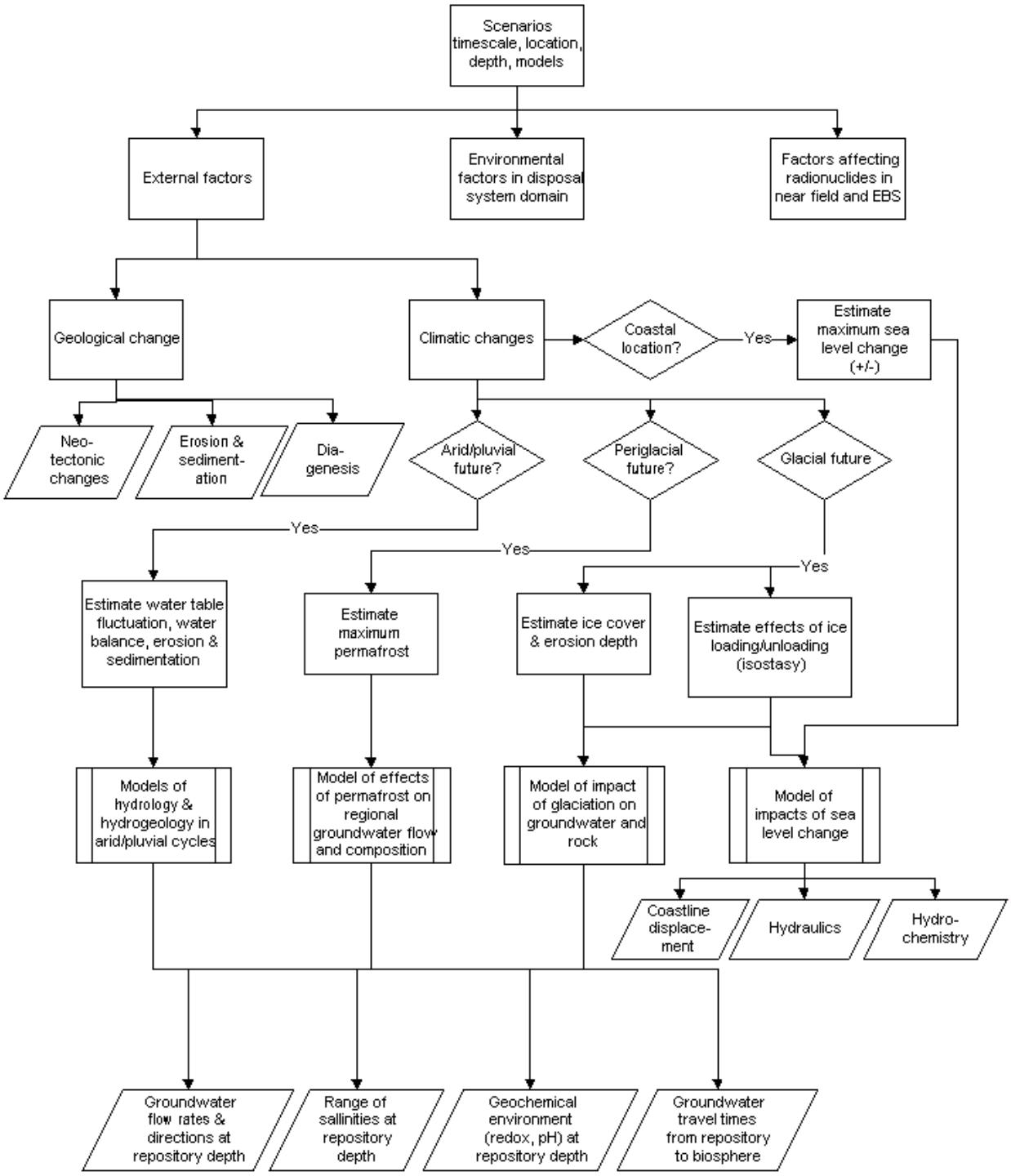


Figure 26. Flow chart showing how scenarios are described in terms of EFEPs (in rectangular boxes) that can be linked with palaeohydrogeological information and other palaeoindicators (in diamond-shaped boxes) via interpretative models (rectangular boxes with double sides).

For example, an outcome of palaeohydrogeological investigations can be envisaged whereby they would show that climatic and other environmental changes over a relevant timescale in the past have not affected the host rock formation and groundwater system at repository depth at a particular site. A more likely outcome, as exemplified by PADAMOT studies, is that there are

lines of evidence with varying weights that suggest some changes at repository depth, and in this case numerical simulations will be required to evaluate their significance for safety. The usual approach for sensitivity analyses has been to choose 'conservative' values for parameters that should result in an over-estimate of risk though the reliability and transparency of assumptions involved in this depend on the conceptualization of the system. Palaeohydrogeological methods, coupled with the development of robust quantitative interpretative models, will reduce the need for conservatism and improve the scientific understanding that underpins the conceptualization of time-dependent changes.

With these reasons as starting points, a generic approach can be suggested for increasing the way that palaeohydrogeology can be used to support PA, or at least for ensuring that information is not lost from the overall safety case.

It is recommended that the most effective way to channel information from palaeohydrogeology into performance assessments is by translating the evidence explicitly into 'external' FEPs (EFEPs; Figure 26). These EFEPs are important in scenario development for PA because they provide information about boundary conditions of the groundwater model and about the chemical properties of the geosphere, redox, pH and salinity, to which near-field conditions and radionuclide mobility may be most sensitive. To transfer this information effectively, it is necessary to appreciate how assessment experts use the FEPs to describe scenarios and where in that process are the qualitative and quantitative interpretative models that would be constrained with palaeohydrogeological information. The proposed method of using palaeohydrogeological information requires that (i) the construction of scenarios by the assessment modelling group is done to assess the possibilities for climate-driven disturbance of the system, and (ii) the interpretation of palaeohydrogeological information by the site characterisation group is more quantitative and explicit in evaluating its significance for the FEPs and the associated uncertainties.

More details of this process for using palaeohydrogeological information are shown in the Technical Report for WP5, which explains how geochemical and mineral measurements from site characterisation should be put through a systematic interpretation (quantitative, qualitative and expert judgement) to obtain data that are comparable with outputs from the scenario models. A supplementary approach is also shown, whereby site characterisation data are used specifically to consider whether there is palaeohydrogeological evidence that climate impacts in the past have been attenuated with increasing depth. If that could be shown, it would build confidence in general principle for geological repositories that deep emplacement in the geosphere will mitigate impacts of future changes at the surface.

7.4 INTERPRETATION MODELS FOR PALAEOHYDROGEOLOGY

The proposed method for considering palaeohydrogeology in PA comprises several interpretative and assessment steps. These will evaluate palaeohydrogeological information in the specific contexts of PA requirements and of scientific knowledge and models. Quantitative data or qualitative information will be the outputs from geochemical and mineralogical methods and will provide varying degrees of constraints on the past impacts of FEPs. This information will, preferably, be placed in a chronology that enables it to be linked to the known timescales of climate-driven EFEPs that affect boundary conditions on a groundwater system:

- Glaciation – injection of meltwater below warm-based ice sheets or from periglacial ice lakes. Geochronology should correlate with a period of glacial advance or retreat.
- Permafrost – reduction of general infiltration and recharge, localisation of discharge, possible salination of shallow groundwater. Geochronology should correlate with prolonged periods of periglacial conditions prior to glacial maxima.
- Arid/pluvial cycles – large fluctuations of recharge and of water table position in southern and central Europe regions. Geochronology may correlate approximately with glacial

periods experienced in northern Europe. Processes with datable indicators may include deep oxidative weathering, secondary mineralisation at water table, episodic salinization, evaporite minerals.
- Sea-level change and shoreline displacement - intrusion of marine water into coastal aquifers, secondary mineral precipitation and/or karstification in mixing zone.
- Neotectonic activity – reactivation of faults and precipitation of secondary minerals, movement of fresh/saline groundwaters and interfaces (in reality, these processes are probably indistinguishable from other processes driven by climate factors).

Geochemical and mineralogical data are obtained by measurements at the site of interest and are interpreted to produce information about past groundwater conditions. Interpretative methods vary from quantitative geochemical models to qualitative expert judgement:

- Groundwater chemical compositions and stable isotope ratios are interpreted to obtain information about the component water origins by graphical techniques, reaction-mixing modelling and statistical modelling.
- Isotopic data related to water ages are interpreted by calculations that involve estimates or assumptions about initial compositions (A_o at $t = 0$), dilution due to water-rock reactions, and in situ production of isotopes.
- Minerals assemblage (i.e. paragenesis) data are interpreted by expert judgement of the environment in which the minerals are stable.
- Geochemical compositions of bulk minerals and of individual growth zones are interpreted semi-quantitatively by stability diagrams or by other methods that relate mineral composition to co-existing solution composition.
- Isotopic compositions of minerals are interpreted for stable isotope fractionation to obtain co-existing groundwater compositions; U-Th data are interpreted to obtain mineral ages by parent-daughter isotope system calculations for which various assumptions are necessary.

These interpretations are likely to produce palaeohydrogeological information that relates to limited spatial and temporal intervals. They are unlikely to produce a coherent and detailed model of evolution of the whole groundwater system over the timescale of interest – the integration of the various bits of information is an interpretative task in which expert judgement inevitably has an important role. In general, interpretation of groundwater data (chemistry and isotopes) identifies the major water components in terms of their typical compositions, sources and ages. Interpretation of mineral data relates to localised geochemical conditions during a discrete interval of mineral growth (or several intervals that may or may not be contiguous). There are many sources of uncertainties in the interpretations of geochemical conditions, of time intervals for which the evidence applies, of the spatial variability, and of the relationships to groundwater movements. Expert judgement is necessary to assess the uncertainties and to consider the possibilities for alternative models. Forward modelling of geochemical processes from hypothetical or typical starting conditions may be valuable as a simplified simulation of the evolution of the real system.

The resulting palaeohydrogeological information can be divided into five categories:
- Groundwater flow rates and directions in the past (though direct evidence of this is rare);
- Ranges of salinities in the past;
- Geochemical environment, especially with respect to pH and redox;
- Groundwater sources and ages, solute residence times;
- Degrees of groundwater mixing.

This information may be directly comparable with the outputs from hydrogeological and geochemical models that are used in developing PA scenarios. This is a basis for using

palaeohydrogeological information as a way of testing whether the system variability introduced by scenario analysis is appropriate for that particular site.

There are many sources of uncertainty in how geochemical and mineralogical data are related to information on EFEPs. Uncertainties in palaeohydrogeological interpretation can be categorised broadly into those originating in data and those associated with interpretations. If palaeohydrogeological information is to be used to describe EFEPs and to construct scenarios for PA, then the uncertainties and probability of occurrence should be clear for the users.

Interpretative models (conceptual and/or numerical) are invariably involved in the palaeohydrogeological interpretation of indicator data. The types of models are exemplified as:

- Geochemical equilibrium models of water-rock reaction;
- Hydrochemical mixing models;
- Hydrological water balance models relating climate variables with groundwater recharge;
- Groundwater flow and mass transport-reaction models to simulate effects of changing hydrogeological and/or geochemical initial and boundary conditions;
- Isotopic fractionation factors;
- Calculation of groundwater ages from isotopic data.

Geochemical equilibrium models are the basis for interpretations that particular minerals or mineral assemblages are indicators of specific hydrogeochemical conditions, e.g. Fe oxide occurrence is equated with oxidising conditions and pyrite, FeS_2, is equated with reducing conditions. These may be oversimplistic interpretations and more rigourous interpretations can be achieved by using geochemical speciation and equilibrium calculations to test equilibria for specific water compositions and mineral phases. This approach has been used in WP4 to evaluate the relationships between Fe and Mn concentrations, mineral assemblage and redox conditions. The main source of uncertainty in the use of a geochemical model is the initial conceptual model, i.e. the mineral equilibria and solution species that are included, and the assumption concerning water-mineral equilibrium. The assumption of local equilibrium being achieved by water-mineral reactions often has uncertain validity but is usually used because of the uncertainties in parameterising reaction kinetics. Thermodynamic data, especially for complex mineral phases, may also be a source of uncertainty.

Hydrological water balance modelling is a particularly significant aspect of palaeohydrogeology in arid climate conditions. This type of model, as demonstrated in WP4, relates recharge rate, i.e. the upper boundary condition of a palaeohydrogeological model, with palaeoclimate. Uncertainty in estimated recharge rates derives from the models for climatic dependence of evapotranspiration and run-off. That uncertainty is propagated into palaeohydrogeological model simulations of water table position, hydraulic gradients and flow rates. The net effect on the parameters for the EFEPs of a groundwater system is illustrated by calculations in WP4.

Coupled models of groundwater flow, mass transport and geochemical reaction illustrate how uncertainties in both hydrological and geochemical parameters are propagated into palaeohydrogeological simulations of hydrochemical evolution and precipitation of secondary minerals. $CORE^{2D}$ modelling in WP4 shows how hydrogeochemistry and hydrogeology are coupled in the system at Ratones, illustrating that spatial variations of geochemical and mineralogical indicators are dependent on the flow regime, so that variability in the later will have influenced the former. PRECIP modelling of secondary calcite growth in a mixing saline groundwater system as at Sellafield reaches similar conclusions.

Stable isotopic ($^{18}O/^{16}O$) fractionation has been used as a palaeohydrogeological indicator of groundwater origins in WP2 studies at Sellafield. Oxygen isotopic fractionation between water and secondary calcite is also a function of temperature, and this dependence introduces significant uncertainty into interpretation of the isotope ratio in terms of groundwater origin and age.

Uncertainty in the model interpretation of groundwater ages from isotopic data (^{14}C, ^{36}Cl, etc) derives from a number of assumptions that have to made about initial isotope abundances and subsequent geochemical and physical processes that might have reduced (or enhanced) the isotope concentration in parallel with radioactive decay. Except in special circumstances in which the parameterisation of the interpretative model is particularly reliable, the uncertainty range in groundwater ages is likely to be between 0.5 to 5 times lower or higher respectively than the 'most likely' estimate, tending towards greater uncertainty at lower isotope abundances, i.e. higher ages. The complexity of dispersive groundwater mixing as age increases means that interpreted isotopic 'ages' have more complex hydrodynamic significance in terms of alternative hydrogeological models.

7.5 SCREENING OF EFEPS WITH PALAEOHYDROGEOLOGY

The preceding paragraphs discuss the scientific background that relates EFEPs to palaeohydrogeological interpretations of geochemical and mineralogical data, and the associated uncertainties. It is clear that there is a large dependence on interpretative modelling and expert judgment. The next step in using palaeohydrogeological information for PA is to consider what approaches might be used to assess the validity and potential significance of EFEPs in scenarios for PA against that information.

Two basic approaches are considered here: firstly the procedure of interpreting geochemical and mineralogical data, preferably using quantitative models or calibrations, and then using expert judgment to draw conclusions of relevance to EFEPs from each individual line of evidence. For example, the data obtained in WP2 lead to inferences about past changes, or conversely about stability, in salinity, redox and other aspects of the hydrochemical environment. This is the procedure that has been used in past instances of using palaeohydrogeology in support of PA.

A second approach is a more systematic 'screening' of EFEPs against palaeohydrogeological information using a formal method for evaluating and weighting evidence. Evidence Support Logic (ESL) is a procedure for doing this (Egan and Bowden, 2004). A small pilot study has used ESL to assess the proposition that 'climate-driven changes over the Quaternary have had little impact at repository depth', using the subset of palaeohydrogeological information for Sellafield in WP2.

Using both of these two approaches, the information about palaeohydrogeology from WPs 2 and 4 has been used to screen the validity and significance of external FEPs (EFEPs) that influence PA. The first approach, using interpretation and judgement of specific information, is discussed in the next section. The second approach, structured evaluation of evidence using ESL, is described in the WP2 report.

Interpretation and judgement of geochemical and mineralogical data and of geochemical modelling have been focused on two key questions that are of direct importance in screening EFEPs for PA:

- What changes, that are not a simple extrapolation over time of what is observed in the present-day groundwater system, affect groundwater compositions and movements over a timescale comparable with the assessment timescale?
- To what degree is the impact on the groundwater system of long-term environmental changes at the surface attenuated with increasing depth?

Palaeohydrogeological information from each of the PADAMOT research sites will be evaluated against these questions.

8 Evaluation of PADAMOT Output

8.1 LOS RATONES AND PADUL/CÚLLAR-BAZA, SPAIN

The main objective of palaeohydrogeological research at the Los Ratones Uranium Mine site was to study the impact of past environmental conditions at the theoretical depth in granite of a high-level waste repository. It is located in the Albalá granitic pluton in the southwest of Spain which has experienced fluctuating aridity and water table elevation in the past. The specific objective for PADAMOT studies was to obtain site-specific data on shallow and deep fracture-filling minerals which could potentially provide a record of the groundwater evolution in this area. Hydrochemical and minerals data have been used for palaeohydrogeological interpretation and modelling.

The strategy followed was:

- To analyse the composition of deep subsurface waters flowing through fractures because of the potential information that it can provide on the geochemical and hydrological evolution of the system. In particular, this could provide an understanding of the major chemical processes which control water composition flowing through fractures in this area.
- To determine the mineralogical and chemical composition of secondary minerals, including fracture-fillings, and to determine their spatial distribution and relationship with groundwaters. Special emphasis has been placed on characterising the carbonate minerals in the system.

The youngest stage of the secondary minerals paragenesis found in boreholes SR-3 and SR-5 at Los Ratones comprises low abundances of calcite and ankeritic (i.e. Ca-Mg/Fe) carbonate. The carbonate minerals show some zoned growth but this is the only direct evidence of fluctuating conditions during precipitation of these late stage minerals sufficient to cause variations in Fe and Mn contents. There is also minor U mineralisation, showing that conditions have at some time facilitated remobilisation of U from primary mineralisation. A U-Th age on one sample indicates an age in the order of 200,000 years, supporting the relevance of these processes to the PA timescale.

Palaeoenvironmental evidence from geochemical proxies at the Cúllar-Baza and Padul research sites has enabled a clearer link to be established between climate change and hydrological conditions. The range of $^{18}O/^{16}O$ ratios in calcite from ostracods in the lower-to-mid Pleistocene sequence in the Cúllar-Baza Basin is 16 ‰, indicating a large effect of evaporation during warm episodes as well as of direct terrestrial temperature variation between glacial and interglacial periods. Moreover correlation of $\delta^{18}O$ and $\delta^{13}C$ in these calcites suggests that the basin is endorheic and that its basic hydrological and hydrogeological character changed through the Pleistocene. A similar picture emerges from organic geochemical proxies and $^{13}C/^{12}C$ for the Padul peat sequence which covers an earlier part of the Quaternary than Cúllar-Baza. In the early-to mid-Pleistocene (1 Ma to 400 ka), a wet climate prevailed, with deeper surface waters and runoff likely to enhance recharge to groundwater. After that, up to the northern latitudes deglaciation at 180 ka, conditions alternated between wetter and drier. In the recent glacial cycles from 170 ka, cold episodes and subsequent deglaciations corresponded with wetter conditions and the Eemian interglacial corresponded with arid conditions. Thus it is certain that recharge to groundwater has varied over the long term and that there were periods in the past (e.g. around 10 ka ago) with lower recharge that at present.

The pattern of alternating ‘warm-arid’ and ‘cold-humid’ episodes in the Iberian Peninsula is quite different to the climate-hydrology relations in northern Europe, where relatively arid conditions were associated with the prolonged periods of permafrost during glaciations. The

information from Cúllar-Baza and Padul provides a strong qualitative confirmation of the water balance modelling approach using the VISUAL-BALAN code to estimate time-dependent variability of recharge as a boundary condition for the groundwater flow and reactive transport model of the Ratones groundwater system.

Modelling of the Ratones fracture-dominated groundwater system shows that the rate of secondary calcite precipitation, the balance between dissolution and precipitation for both calcite and silica, and the penetration of oxidising conditions versus precipitation of pyrite are all sensitive to recharge rate. Modelling also suggests that redox conditions are likely to be buffered by the pyrite-goethite (Fe-oxide) couple at the depths of investigation. Siderite dissolves under those conditions and the model suggests that siderite budget may influence switches in redox conditions corresponding to recharge rates and thus also to climate changes. At greater depths, pyrite dominates redox control in the model and thus Eh is likely to be more negative.

These modelled variations in the systems can be compared with the evidence from site investigations. The dominant secondary minerals at Ratones are clays, mostly smectite, and carbonates are found mainly in core samples from intermediate and deep boreholes (SR-4 and SR-5) in the southern, down-gradient, part of the system. Present-day groundwater compositions are generally consistent with the secondary mineral distribution, so there is not recognisable evidence of distinctive palaeohydrogeology in the mineral assemblage. Indeed the up-gradient part of the system is found to be dominated by dissolution reactions by which pyrite and ankerite carbonate are being progressively removed from the fracture assemblage, and only in the down-gradient part is there evidence that Fe-rich carbonate may be actively precipitated.

Evidence about redox conditions is also mainly limited to the present regime, there being only weak indications of compositional zoning in carbonates and sparse pyrite in borehole SR-5 down to 500m depth. The relationship between uranium mineralisation in fractures and dissolved U in groundwaters is similarly controlled by dissolution and hydrodynamic mixing, and the chronology and palaeohydrogeological conditions that have controlled secondary U mineralisation are not clear.

Groundwaters with ages from very recent to more than ten thousand years are present in the system, but palaeohydrogeological information from secondary minerals and the hydrochemistry itself do not contain clear signals that link with the palaeoclimate and hydrological record from Cúllar-Baza and Padul. However a general assessment of all of these various types of information indicates that EFEPs for PA scenarios at this type of site should include depth-dependent and time-dependent variations of flow, hydrochemistry and possibly also redox.

It is considered that, apart from the anthropogenic changes due to the mine itself, the greatest possibility of discontinuous change in the groundwater system would be fluctuations of the water table and hydraulic gradient synchronously with arid-pluvial cycles of climate. Site investigations have concluded that mineralogy is not a substantial source of evidence for hydrodynamic changes and provides only scant evidence for geochemical changes. Most of the groundwater system that has been investigated so far comprises a slowly weathering geochemical environment, dissolving calcite and not precipitating it. Therefore calcite, which is the main focus of secondary mineral studies in PADAMOT, is not a viable source of palaeohydrogeological information here. The extent to which groundwater conditions have fluctuated over time is not evident from this or other types of geochemical data. Data from chemical and isotopic analyses of groundwaters, carried out outside PADAMOT, are also not explicitly diagnostic of palaeohydrogeology although they assist in identifying the structural controls on flowpaths and hydrochemical mixing in pre- and post-mining groundwater regimes at Ratones.

Geochemical proxies at the Cúllar-Baza and Padul sites are a successful tool in the context of Spanish sites for diagnosing evidence of regional hydrological impacts of past climates. Stable O and C isotopic ratios in calcite from ostracods and organic geochemistry proxies identify those impacts very clearly and moreover can be placed in a discrete chronological sequence due to the

success of dating techniques and to the completeness of the Cúllar-Baza and Padul sequences. Stable O isotopes also indicate clearly that intense evaporation has occurred at certain periods, which can be inferred to correspond to episodic water table fluctuations and variations of water compositions. This is valuable input to the VISUAL-BALAN model of time-dependent variations of recharge.

Overall, it can be concluded that the mineralogical and geochemical methods promoted by PADAMOT have not been useful in the shallow weathering regime at Los Ratones. Palaeohydrogeological evidence has not yet been able provide significant support to the successful development of integrated theory-based time-dependent modelling of the groundwater system. However the methods might be useful in any future testing below presently-investigated depths at this type of site to investigate how deeply oxidising and dissolving geochemical conditions have penetrated at different times.

8.2 ÄSPÖ AND LAXEMAR, SWEDEN

In the previous EQUIP palaeohydrogeological project, samples collected mainly from Äspö drill cores were studied. PADAMOT investigations have focussed on mineralization from borehole KLX01, which was drilled down to 1070 m depth at Laxemar.

The postglacial evolution of the area has been strongly influenced by a complex interplay between global sea-level changes, fresh water run-off from the surrounding terrain, and glacio-isostatic fluctuations in the land surface. Consequently, the sites have experienced several different episodes during which either fresh or brackish water environments developed after the last glaciation, and which have had a large influence on the present groundwater chemistry.

The following evolution of groundwater through the Quaternary glaciations and the Holocene deglaciation starting at 13,000 to 14,000 years BP has been inferred from interpretation of their chemical and isotopic compositions:

- Deep recharge by glacial melt water due to high hydraulic heads in the ice sheet and groundwater mixing at considerable depth with a saline water of brine-type.
- Brackish/saline water has been introduced by density turn-over at various stages of the pre-Baltic (Yoldia and Litorina) and Baltic Sea. The present-day brackish water conditions of the Baltic Sea were established around 2,000 years BP and have remained constant to the present day.
- Since Äspö rose above sea-level at around 4,000 years BP, meteoric water has been recharged and mixed with the earlier mixed groundwaters.

Previous stable isotope analyses of secondary calcites at Äspö, including those reported in the EQUIP project, found low temperature calcites precipitated from brackish and marine waters down to depths of around 500 m. Small amounts of calcite that had possibly precipitated from meteoric groundwaters containing components of somewhat colder climate waters (i.e. portions of glacial meltwater) were detected at greater depths, possibly down to 1000 m. New studies in PADAMOT suggest that meteoric water penetration might have been even deeper at Laxemar than at Äspö, whilst brackish-marine water penetration was less deep. This is consistent with observations of the present-day hydrochemistry and also with palaeohydrogeological inferences based on the hydraulic effects of land uplift and shoreline displacement. However it is notable that, unlike data from Äspö, stable isotopes have not indicated the presence of calcite with a significant cold climate water signal in deep samples from Laxemar. It is now thought possible that the EQUIP data for Äspö calcites might have overestimated the cold climate water component, due to poor drillcore quality and the lesser use of morphology to select samples that are representative of late stage calcites. The present study has further emphasised the importance of integrating stable isotopes, Sr isotopes, morphology and compositions in the interpretation of whether calcites have late-stage (i.e. Quaternary) origins. Mistaken identification of

hydrothermal calcites as late stage calcites puts erroneous weight on the evidence for cold climate waters in the past.

The latest stage of the secondary minerals paragenesis in Laxemar borehole KLX01 comprises small amounts of euhedral calcite, ± pyrite, small quantities of clays (chlorite, etc) on the outermost surface of potentially-conductive fractures, which are mostly partially filled with much earlier mineralisation hydrothermal, and Fe-oxide in near surface (<50-100 m) samples. Caution is, however, required when interpreting this assemblage – it is probably a discontinuous record of groundwater conditions that over-represents the 'precipitating' periods of hydrochemistry, as opposed to 'dissolving' periods. Local redistribution of secondary minerals by dissolution-reprecipitation, probably facilitated during periods of microbial viability and activity, is also thought to be a factor behind what has been observed.

It is suggested that variations in microbial activity over time and with depth is a significant factor in hydrogeochemical conditions. This is likely to be related to the variation over time and depth of traces of dissolved organic carbon in the system. Propagation of microbial activity and trace organics to intermediate depth at some times in the past is confirmed by low $\delta^{13}C$ values in secondary calcite and by the variability of trace elements Mn and La with depth. The significance for past geochemical conditions of variable CL luminescence among growth zones in secondary calcite, which corresponds primarily to variations in Mn content more than in Fe content, needs to be examined in the context of the modelling carried out in WP4. Overall, the mineralogical and isotopic data suggest that EFEPs should include variability in these complex controls on groundwater compositions possibly including redox, over time and probably down to repository depth though this will depend on the overall groundwater flow regime.

Interpretation of calcite morphologies at Äspö/Laxemar is presently based on an assumption that these variations have the same correlation with salinity as has been established at Sellafield, and also on an assumption that the age of the secondary calcite is within the timescale over which fluctuating palaeohydrogeological conditions would be relevant. Variations of late-stage calcite morphology are greater over the upper 260 m of the Laxemar borehole than was recorded from Äspö samples, suggesting that salinity down to this depth at Laxemar was variable in the past. There are very few samples from 260 to 800 m at Laxemar and those few samples tend to correspond to fresh water conditions, but comparisons are not justified. Movement of the position of the fresh-saline interface at Laxemar should therefore be considered in the screening of EFEPs for scenarios in a safety case. Moreover the localisation of changing calcite morphologies within fracture zones suggests that transmissivity of these zones has a stability and longevity, though the timescale is not quantified. Thus continual fracture re-activation is supported and an EFEP of time-dependence for fracture transmissivity might be discounted in this case.

Of particular interest at borehole KLX01 is the existence of calcite with fresh water morphology in a steeply dipping fracture zone at 840-950 m, at which depth present groundwater is saline. This is clear evidence of past deep penetration of fresh water which contributes to an EFEP describing time-dependent changes of groundwater flows in response to uplift and shifting shoreline. It is not a surprising observation in the light of fresh water existing presently at comparable depth in the nearby borehole KLX02. The paragenesis of secondary minerals analysed in samples from 910 m, comprising successive episodes of calcite precipitation from saline groundwater, calcite dissolution and minor clay formation, and further calcite precipitation in fresh water, also indicates that hydrodynamic change even at depth has proceeded as a smooth evolution. Stable isotopic compositions of fresh water calcites from 800-950 m depth in KLX01 indicate that they did not precipitate from a fresh water of dominantly cold climate origin, although this does not preclude minor components of such water.

Palaeohydrogeology offers much information to support EFEP definitions for this site. It is evident that groundwater salinity has changed over time at the depths of particular interest for PA, especially where steeply-dipping fracture zones provide transmissive connections from

surface to depth. Whether deep fresh water incursions here involved dominant portions of cold climate waters at some times in the past is not clear. Stable isotopic compositions of secondary calcites do not so far record such an episode, although present-day groundwaters are known to retain a minor component of cold climate water. The range of fluctuations of other hydrochemical conditions, especially redox, is also unclear: compositional zoning is not apparent in calcite, though the low quantities prevent definitive analysis, and redox-related evidence of microbial activity, biogenic dissolved inorganic carbon, Mn and La suggests some fluctuations down to about 600 m depth. The persistence of pyrite in the late stage assemblage suggests that any fluctuations have been limited within a range of generally reducing conditions though an EFEP should consider the possible implications.

Mineralogical and isotopic properties of secondary calcites are distinct in the brackish-marine and meteoric-?glacial groundwater regimes at intermediate depths and deep locations respectively in the Äspö and Laxemar systems. The resulting information about past distributions of groundwater masses supplements the palaeohydrogeological interpretation of sampled groundwater compositions by qualitatively indicating the sensitivity of these distributions to temporal changes of boundary conditions. This provides valuable input to scenario development, but its qualitative nature limits its value for testing the validity of palaeohydrogeological modelling. Data are primarily limited by the sampling limitations and challenges imposed by sparse secondary minerals. Two cautionary comments on the PADAMOT methodology are that interpretative models for morphology variations are presently generic and rely on calibrations of morphology versus salinity in Sellafield calcites, and that secondary minerals provide a discontinuous record which omits periods of mineral dissolution. It has been observed that late-stage secondary calcites are localised in certain fracture zones, with different calcite generations distinguished by their morphologies. This is significant for PA in showing the persistence over time of the spatial distribution of water flow paths.

Overall, the PADAMOT methodology for palaeohydrogeology provides some important indications of the breadth of variability that PA scenarios should consider for the Laxemar/Äspö groundwater systems. As in the Sellafield case below, a quantitative output to interpretative models such as those in Figure 3-2 is, however, not possible.

8.3 SELLAFIELD, DOUNREAY AND CLOUD HILL, UK

Detailed petrological studies of the fractures and associated mineralization were carried out for Nirex and also as part of the EQUIP palaeohydrogeological investigations. These studies demonstrated a close relationship between the distribution of late-stage calcite fracture mineralisation and present-day groundwater flow. The morphology and microchemical characteristics of the calcite vary systematically with groundwater salinity, and could be used to differentiate calcite precipitated in freshwater and saline water. Morphological and fluid inclusion evidence suggested that the bulk of the late stage calcite formed from groundwaters similar to those at the present day, however detailed petrographical analysis of growth zones in calcite from the freshwater-saline water mixing zone indicates changes of morphology during calcite growth. It was concluded that the morphology of calcite as it has grown is an indicator of the evolution of groundwater salinity especially at the mixing zone between fresh and saline water masses and thus is an indicator of the long-term hydrodynamic stability of the groundwater system.

PADAMOT studies sought to test whether the relationships between these characteristics of late-stage calcite and groundwater chemistry that are observed at Sellafield are also useful for palaeohydrogeology at other sites. The specific objectives of the studies were to:

- Evaluate further the relationships between late-stage calcite mineralisation and the evolution of the modern groundwater system at Sellafield;

- Compare relationships between late calcite and groundwater compositions at Sellafield with those at other UK sites, to evaluate their application as a more generic palaeohydrogeological tool.
- Investigate whether calcite mineralisation associated with the development of present-day deep groundwater system records the impact of past climatic changes during the Quaternary.

Secondary calcite mineralizations were also sampled from a deep borehole that had been drilled at Dounreay in northern Scotland and from Carboniferous Limestone at Cloud Hill in the English Midlands.

8.3.1 Sellafield

Late-stage calcite occurs most commonly in fractures in both the Permo-Triassic sedimentary rocks and the Borrowdale Volcanic Basement rocks in the eastern part of the Sellafield area. Its occurrence is limited in the western part of the area where the rocks dip underneath the coast. Morphologies of late stage calcites that are revealed by luminescence zoning in CL studies suggests, in the predominant number of late stage calcites studied, that the fresh-to-brackish water transition has been shallower in the past, i.e. the salinity has decreased over time. Observed morphologies in a few late stage calcites suggest that the opposite has been the case, i.e. the fresh-to-brackish groundwater transition has been slightly deeper in the past and that the salinity in this depth interval has increased over time. These apparently conflicting pieces of evidence may be explained as the result of fluctuating location of the saline transition zone and different calcites having grown over different time intervals. The overall palaeohydrogeological significance seems to be that hydrodynamic conditions have fluctuated either side of present-day hydraulic gradients, at least in the shallow part of the system above the saline groundwater body.

Geochemical variation and growth zoning (as revealed by CL) in calcite indicate that geochemical conditions fluctuated over time and were more localised in up-gradient locations in the eastern part of the area and above the saline transition zone. Geochemical changes deep in the saline groundwaters are represented by fewer CL-distinctive zones that are replicated in samples from several boreholes, i.e. they represent more general geochemical changes. Fe and Mn variations do not have clear relationships with the degree of CL activity, though overall Fe and Mn are much higher in calcites in saline conditions than those above the saline transition zone. There is also a clear correlation in freshwater calcite between low CL activity (i.e. non-luminescence due to low Mn and Fe) and low concentration of the REE cerium ('Ce anomaly'). In summary, these data from CL and trace element (Fe, Mn, Ce) analyses indicate that redox conditions have undergone changes that have probably been fairly substantial in the shallower, fresh water parts of the groundwater system. There have also been changes in the deeper system, as indicated by CL, Fe and Mn variations, but these changes have probably had smaller ranges of variation. The magnitude of redox variation cannot be quantified uniquely from Fe and Mn data, as explained by the modelling carried out in WP4 of PADAMOT, but these data plus consideration of Ce data suggest that fluctuations of redox in the deep saline groundwaters have been within a range that has remained generally 'reducing'.

Some fluid inclusions have higher salinities that present co-existing groundwaters, but inferences that these are hosted in very old growth zones of late stage calcite casts doubt on the palaeohydrogeological significance for the timescale of interest.

Successful microanalyses of the stable isotopic compositions of discrete growth zones, especially those for $\delta^{18}O$ using the ion microprobe, provide perhaps the most compelling palaeohydrogeological information. There is some correlation between CL activity and $\delta^{18}O$, the brighter growth zones, which tend to be older, having relatively depleted ^{18}O. However doubt remains about whether these growth zones represent a relevant timescale. The depleted ^{18}O calcite zones are identified at about 200m depth (ion microprobe data) and at 400-900 m depth (He-LACE data with poorer spatial resolution and non-specific correlation with zones). These

isotopic compositions suggest that the zones grew from waters that had large proportions of glacial melt water. It is noteworthy that the spread of $\delta^{18}O$ compositions at 900 m depth goes to heavier ^{18}O values consistent with present water composition, as do ion microprobe analyses of calcite from 1500 m depth. These suggest that glacial meltwater did not penetrate substantially below 1000 m. Conversely, the data indicate that water below 1000 m may have been mostly similar to present-day groundwaters over the period of calcite growth.

Variation in the $\delta^{18}O$ values for calcite growth zones above the saline transition zone indicates clearly that there have been large palaeohydrogeological variations in the present fresh water zone.

In conclusion, these additional geochemical analyses for Sellafield samples consolidate the interpretations that were possible from analyses in the EQUIP project. However they have also highlighted some of the uncertainties and ambiguities in the timescale represented and the palaeohydrogeological information. The information is essentially qualitative, showing that the groundwater system has changed in the past and that the sensitivity to external changes generally diminishes with increasing depth. The evidence relates specifically to the impacts of external changes on 'turnover' of the groundwater volume, groundwater salinity and contents of redox-sensitive trace elements (Fe, Mn, Ce). However it is also evident that water with cold climate origin (e.g. glacial melt water) has penetrated to around 1000 m in substantial quantities in the past. There is also uncertainty about the ages and origins of waters that have reached greater depths in the past and that appear to have been isotopically similar to present water at these depths. The exact significance in terms of redox changes of evident temporal and spatial variations of Fe, Mn and Ce in calcite growth zones and thus in co-existing palaeogroundwaters has various uncertainties (as explained for Fe and Mn in the WP4 report). It is most likely that the observed changes of Fe and Mn contents and in Fe:Mn ratios reflect redox changes that have been induced by hydrodynamic and hydrochemical changes originating in recharge. The magnitude of redox change is attenuated with increasing depths. The geochemical indications of redox also have to be interpreted in the context of other redox indications and agents, notably mineralogy, in this case the localised occurrence of pyrite, and microbial intervention.

Additional petrographic analyses of late stage calcite in drillcore samples from past site investigations at Sellafield in northwest England have consolidated the findings from previous work carried out in the EQUIP project. Morphology variations in overgrowths of late stage calcite have suggested that the position of the fresh/brackish-to-saline water transition zone has fluctuated both above and below its present location, but with additional observations the balance of evidence supports the predominance of a slight downward movement, by at most a few tens of metres, of the transition zone over time, i.e. a dominant trend over time of decreasing salinity at any point in this interval. This indicates that a hydrodynamic and hydrochemical response at 300-400 m depth to changes in the surface environment should be considered in FEPs, but also that the distributions of flow directions in the groundwater system has remained fairly stable over the time period represented by the late stage calcites. Data from various instrumental methods for analysing chemical and isotopic compositions of discrete calcite growth zones suggest that the compositions of groundwaters from which they precipitated changed over time. The patterns of variations support the concept that changes in deep saline groundwaters are more attenuated than in fresher up-gradient groundwaters. In these freshwater calcites, contents of the redox-sensitive trace elements Fe, Mn and Ce are correlated which indicates that the fluctuations in compositions are related to changes in palaeoredox conditions. Thus palaeohydrogeological information suggests that FEPs for PA should consider long-term changes of redox, although it is also evident that the scale of change is attenuated in deeper saline groundwaters. The quantitative significance of the observed Fe and Mn variations has been studied in WP4 by geochemical modelling, which shows that absolute and relative changes in Fe and Mn concentrations have non-unique interpretations in terms of redox (Eh) values.

8.3.2 Dounreay

Late stage calcite in much scarcer in fractures in the sedimentary and basement rock formations at Dounreay than in rocks at Sellafield. Consequently its morphology tends to be dominated by older generations of calcite on which it has precipitated as a thin veneer. In such cases, there is much less consistency in the relationship between apparent morphology and salinity and thus less confidence in a palaeohydrogeological interpretation based only on morphology. The interpretation has further ambiguity due to the lack of correlation between the depth of morphological change inferred from mixed and complex data and the depth of the existing fresh to brackish/saline water transition. The former seems to be at around 150m depth and the latter at below 800 m depth. Whether this saline transition zone in groundwater has been at shallower depth in the past is a matter of conjecture and cannot be assessed further by fluid inclusions of which there are none that are measurable with useful certainty in the late stage calcite.

CL activity and trace element (Fe, Mn, Ce) contents are also less helpful as palaeohydrogeological indicators for Dounreay than for Sellafield. Shallow late stage calcite is mostly luminescent under CL and has less trace element variation (and no Ce anomaly) than late stage calcites from Sellafield. There are greater variations of luminescence and trace elements in deeper (>1000 m) calcites from Dounreay but the significance is not interpretable. Moreover the reliability and significance of low salinity fluid inclusions, apparently correlating with low luminescence, are also not interpretable with certainty. The implication is that fresh water penetrated below the present saline transition at some time in the past and perhaps in a localised flow path, but the evidence is too uncertain for this to constitute useful palaeohydrogeological information.

As is observed in Sellafield samples, $\delta^{18}O$ data for Dounreay calcites indicate that glacial melt water penetrated to at least 450 m depth but less substantially at below 1000 m depth. $\delta^{18}O$ of calcite at around 1200 m appears to link it with very old basinal dewatering rather than with groundwaters over a timescale of interest in the present context.

Samples of secondary calcite from Dounreay posed an analytical and interpretative problem because the amounts of late stage calcite are low. The calcite morphologies tend to be dominated by that of older secondary calcite on which late stage calcite has precipitated as a veneer. Uncertainty in calcite characterisation means that the significance of the substantial discordance in the depth locations of the transitions of morphology of late stage calcite and of salinity in the present-day groundwater profile at Dounreay is interpreted with much less confidence than for samples from Sellafield. Variations of redox-sensitive trace elements (Fe, Mn, Ce) are less systematic than at Sellafield although there is a general contrast between trace element contents of shallow and deep calcites with more variation at depth. However there is too much uncertainty and lack of reproducibility in these sparse localised data to interpret reliable palaeohydrogeological information. The few stable isotope data from Dounreay calcites tend to repeat the inference from isotope analyses at Sellafield that glacial or cold-climate water volumetrically replaced pre-existing water down to about 450-500 m depth since late stage calcites below this do not have such light $\delta^{18}O$ values.

8.3.3 Cloud Hill

Observations of calcites that are inferred to be ‘late stage’ demonstrate further the difficulty and uncertainty in making useful palaeohydrogeological interpretations from morphology when the relevant calcite is very sparse and precipitated as a veneer on pre-existing secondary mineralisation. In this case, the pre-existing secondary calcites, and also dolomite generations, are probably related to Palaeozoic basin burial and evolution so are of no relevance for present purposes.

Analyses of redox-sensitive trace elements Fe and Mn, in the late-stage calcite show these to be present at low concentrations and thus probably typical of calcites precipitated in near-surface

oxidising groundwaters. Geochemical modelling in WP4 has confirmed that this is a valid, but not unique, interpretation. These low Fe and low Mn, mostly low luminescence (except for relatively minor zones that have higher Mn and are more luminescent) calcites might be considered as analogues for secondary calcites that are definitely representative of shallow environments dominated by oxidising supergene alteration. However the absence of a Ce anomaly indicates that interpretation of the presence of a Ce anomaly, as in the non-luminescent growth zones in shallow calcite from Sellafield, is not simply a matter of oxidising versus reducing palaeogroundwater. Geochemical conditions in the source regions for groundwaters may have as important a role in determining their compositions as the geochemical environment where calcite has been precipitated.

The rather wide range of $\delta^{18}O$ values obtained by ion microprobe and He-LACE analyses of the late stage calcite, both significantly heavier and lighter than equilibrium with present-day groundwaters, is also an indication of possible uncertainties in the palaeohydrogeological interpretation of such data. Three possible explanations can be proposed: actual variations in palaeohydrogeology in the timescale of interest, 'contamination' of analyses by older calcite, or non-equilibrium isotopic fractionations.

8.4 MELECHOV MASSIF, CZECH REPUBLIC

Melechov has a particular set of potentially-important EFEPs that define present-day and long-term groundwater movements and siting of a potential repository in this type of rock formation and location. Palaeohydrogeology since the Tertiary period, is thought to have been dominated by weathering, hydraulic gradient increase and potential fracture reactivation that were associated with general uplift of the massif. Thus EFEPs need to describe depth-dependent transmissivity in fracture zones and faults, and lateral connections within the fracture network from the topographic high in the centre to potential discharge areas on the periphery, and whether these characteristics have changed over time.

Groundwater ages and other hydrochemical information are the primary source of evidence to define those EFEPs. Isotopic data on groundwater from the borehole at Melechov show that, at this shallow depth range, groundwater is entirely recent recharge and geochemically immature, though some evolution to Ca-Na-HCO_3 composition has occurred. Predominance of a pre-existing fracture mineral assemblage of probable hydrothermal origin that comprises Fe- and Mn- oxides as well as chlorite and pyrite (increasing downwards) indicates that redox-controlling reactions may already be occurring but are not yet buffering redox conditions. In other words, the weathering process between infiltration water and existing fracture minerals and wall rock is likely to advance over time in this hydrodynamically shallow zone.

Information from Melechov is limited because the borehole is only 100m deep, but sparse hydrochemical and isotopic data from other locations in the southern Bohemian Massif (i.e. not in the areas of the northern massif where thermal springs represent connected and transmissive fractures that penetrate to anomalous depths) indicate that the distribution of groundwater ages with depth may be rather heterogeneous. Thus an EFEP describing depth dependence of groundwater movement would need to be left open in the present state of knowledge.

Although this type of site, in the centre of a domed massif, has some potentially important time-dependent EFEPs that might influence scenarios, the PADAMOT methodology is not applicable for the shallow depth interval to which Melechov investigations are presently limited. As is the case for the Ratones site, methods that focus on secondary minerals, specifically calcite, are not practicable for the shallow weathering zone but are likely to become valuable in deeper investigations.

An important aspect of the Melechov massif study is that the general directions of flow paths from recharge to discharge, i.e. from the uplands of the domed massif to the incised rivers at its periphery, are fairly obvious, but the depth dependence of flow and travel times to discharge are

not known at all. These latter properties would of course be of central importance for the siting and PA of a repository sited in this sort of hydrogeological environment. The PADAMOT methodology combined with conventional hydrochemical and isotopic studies could provide valuable information about the deep parts of the down-flowing limbs of the groundwater system and about the flowpaths that converge towards groundwater discharge areas at lower elevation.

9 Conclusions and Recommendations

Palaeohydrogeological information is one of two main sources of supporting evidence to complement quantitative radiological assessment studies, the other one being natural analogues, that are available with which to test or moderate the degree of confidence in hydrogeological and geochemical aspects of a long-term safety case for a geological repository. The work undertaken in PADAMOT has also demonstrated the role that palaeohydrogeology can play in providing confidence in the stability of the geosphere barrier function. There is therefore a strong requirement to carry out palaeohydrogeological studies of a potential repository site in order to demonstrate that the waste management agencies and regulators understand the processes involved and can take account of factors that might affect safety in an appropriate manner.

A safety case must extend for many thousands of years and, for most regulatory frameworks, this is typically up to at least the timescale in which radionuclide releases might reach a maximum. Over that length of time, conditions at the surface will change due to climatic changes and conditions underground may change due to the downwards propagation of surface effects and also due to geologic changes. Conditions at depth where a geological repository would be located are generally less susceptible to change, benefiting from the inherent stability that rocks at moderate depths have in many locations. The lower susceptibility to disturbance and change is one major reason why geological disposal is the preferred option over storage at the surface for long-term waste containment. However that reduced susceptibility to change, and the degree to which a safety case depends on it, need to be tested and demonstrated in the natural geologic system if there is to be confidence in the models on which a safety case is based.

Both the EQUIP and PADAMOT projects focused on geochemical and mineralogical proxies for palaeohydrogeology. It could be argued that these programmes of research have exhausted the potential of such proxies to provide useful information and have identified the limitations of the various methodologies and modelling tools. However WP2 has shown that further progress in characterising proxies and interpreting palaeohydrogeological information is possible with state-of-the-art analytical techniques.

There can be no doubt that future developments in analytical tools will bring about additional improvements in the resolution and sensitivity of mineralogical, geochemical and isotopic analyses and in the reliable quantification of these types of information. However it will remain a matter of judgement as to when enough information has been collected, and this must relate to the safety case objectives. Interpretative modelling will need to develop further the approaches that have been demonstrated in WP4 so that the significance of 'proxy' data for palaeohydrogeology and specifically for information that is useful for scenario development can be realised and calibrated.

Advances in modelling capabilities and computing power will enable proxy data to be better used for palaeohydrogeology. The integration of climate-driven hydrological modelling with reactive mass-transport modelling of groundwaters, via changes of time-dependent boundary conditions, is one of the areas developed in WP4 which offers the possibility of directly linking scenarios for groundwater conditions down to repository depth with climate scenarios in PA. This approach to evolutionary coupled modelling over long timescales matches the advances in PA codes which take into account temporally variable boundary conditions.

This study concludes that the most appropriate way to incorporate more palaeohydrogeological information into PA is to use palaeohydrogeology to screen and quantify FEPs that are the basis for developing scenarios to be used in PA. Logical approaches to doing this have been illustrated in this study, showing the considerable steps of data acquisition, interpretation and expert judgement that are involved in attempting to quantify information for transfer into FEPs and scenarios. The process of interpretation and expert judgement is usually carried out by

means of a narrative assessment of the evidence, supported by geochemical, hydrodynamic and coupled reaction-transport modelling as illustrated in WP4. A more rigourous approach with ESL has been exemplified here but it is likely that the conventional narrative interpretation will continue to be the most practicable approach.

Narrative interpretations have been abstracted from the investigations carried out in WP2 on samples from the various study sites. The principal analytical methods that have been used and evaluated in WP2 are mineralogical, geochemical and isotopic analyses of late-stage secondary calcite. Their applicability depends primarily on the occurrence of late-stage calcite in sufficient abundance for characterisation to be analytically feasible and reasonably reliable. In general, late-stage calcite has grown and been preserved at depths below the weathering zone where groundwater compositions have been continually saturated with respect to calcite. Where these conditions obtain, as at typical repository depths, i.e. below 100-200 m, in the rocks at Sellafield, Äspö/Laxemar and Dounreay, a remarkable amount and diversity of data may be obtainable, though abundance of secondary calcite and the feasibility of sampling are strong constraints on what can be achieved. In other geological and hydrogeological conditions, e.g. in shallow groundwater environments and at earlier stages of site reconnaissance, different sampling and analytical approaches are necessary and are illustrated by the studies at Los Ratones and Melechov.

Even in the most advantageous sampling and analytical conditions, there are substantial interpretative uncertainties associated with the assumptions made in expert judgement and with calibrations of process models. Further basic research to understand the geochemical and mineralogical processes underlying the genesis of secondary calcite, the calcite morphology-salinity relationship, and the distributions of redox-sensitive trace elements in secondary minerals is required to reduce these uncertainties. Nevertheless it is evident from these PADAMOT studies that, by adopting palaeohydrogeological methods that are appropriate to the particular geological and hydrogeological conditions, important qualitative evidence of greater or lesser degrees of stability in past groundwater conditions is already accessible. This ‘palaeo’ evidence should be taken into account in considering scenarios of future climate changes and their potential impacts on the stability of deep groundwater conditions for repository safety cases.

Glossary of Abbreviations

ANDRA	Agence Nationale pour la Gestion des Déchets Radioactifs (France)
ArcView	Geographical Information System software package
ArcInfo	Geographical Information System software package
Ba	barium
Be	beryllium
BENCHPAR	Benchmark tests and guidance on coupled processes for performance assessment of nuclear waste repositories (FP5 project)
bgl	below ground level
BGS	British Geological Survey
BIOCLIM	Modelling Sequential Biosphere Systems under Climate Change for Radioactive Waste Disposal (FP5 project)
BP	Before Present
Br	bromine or bromide ion
BSEM	back-scattered scanning electron microscopy
BVG	Borrowdale Volcanic Group formation (at Sellafield)
C-14	carbon-14 isotope (also ^{14}C)
Ca	calcium
Ce	cerium (a light rare earth element)
CHN	carbon-hydrogen-nitrogen analyser
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
Cl	chlorine or chloride ion
CL	cathodoluminescence microscopy
Co	cobalt
$CORE^{2D}$	computer program for modelling groundwater flow, solute transport and geochemical reaction
Cu	copper
EC	Commission of the EU
EDXA	energy-dispersive X-ray microanalysis
EFEPs	external FEPs
Eh	platinum electrode measurement of redox (usually versus standard hydrogen electrode potential)
ENRESA	Empresa Nacional de Residuos Radiactivos, S.A. (Spain)
EPMA	electron probe microanalysis
EQUIP	Evidence from Quaternary Infills for Palaeohydrogeology (FP4 project)
ESL	Evidence Support Logic

Eu	europium
EU	European Union
Fe	iron
FEPs	Features, events and processes
FP4	the EU's 4th Framework Programme of RTD
FP5	the EU's 5th Framework Programme of RTD
FT-IR	Fourier transform infrared spectroscopy
FTP	file transfer protocol
GIS	Geographical Information System
He-LACE	helium-flushed laser-assisted carbonate extraction
Hf	hafnium
HREE	heavy rare earth element
HRL	Hard Rock Laboratory (at Äspö, Sweden)
ICP-MS	inductively-coupled plasma source mass spectrometry
K	potassium
ka	thousands of years
ky	thousands of years
La	lanthanum
LAMP-ICP-MS	laser ablation microprobe ICP-MS
Li	lithium
LREE	light rare earth element
m	metres
Ma	millions of years
m a.s.l.	metres above sea level
mbOD	metres below Ordinary Datum (i.e. below sea level)
MENHARD	computer program for groundwater flow modelling
ME9	Mineralisation Episode 9 (late-stage mineralisation in the fracture mineral paragenesis in the basement rocks at Sellafield)
Mg	magnesium
mg/L	milligrams per litre
Mn	manganese
MODFLOW	computer program for groundwater flow modelling
m/s	metres per second
MS	mass spectrometry
MTA	microthermometric analysis of fluid inclusions
MTZ	Morphological Transition Zone
Na	sodium

NAGRA	Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (Switzerland)
Nd	neodymium
Ni	nickel
Nirex	Nuclear Industries Radioactive Waste Executive (UK)
OD	Ordinary Datum (sea level reference for elevation in UK)
PA	Performance Assessment
PADAMOT	Palaeohydrogeological Data Analysis and Model Testing
PAGEPA	Palaeohydrogeology and Geoforecasting for Performance Assessment in Geosphere Repositories for Radioactive Waste Disposal (FP4 project)
PALHY	Cluster of palaeohydrogeology projects in FP4
Pb	lead
PDB	PeeDee belemnite standard carbonate for $\delta^{13}C$ and $\delta^{18}O$
PERMA	research project investigating permafrost at the Lupin mine, Nunavut, northern Canada
PHREEQCI	interactive version of PHREEQC2 with graphical user interface
PHREEQC2	computer program for geochemical modelling of reaction and equilibrium with mineral phases (from the US Geological Survey)
PHYMOL	Palaeohydrogeological Study of the Mol Site (FP4 project)
PFFs	potential flowing features
ppm	parts per million
PRECIP	computer program for modelling groundwater flow, solute transport and geochemical reaction
RAWRA	Radioactive Waste Authority, SÚRAO (Czech Republic)
Rb	rubidium
REEs	rare earth elements
RTD	research, technological development and demonstration
SEM	scanning electron microscopy
SIMS	secondary ion mass spectrometry
SKB	Svensk Kärnbränslehantering AB (Sweden)
Sm	samarium
SMOW	Standard Mean Ocean water standard $\delta^{18}O$ and $\delta^{2}H$
SQL	database system software
Sr	strontium
SSG	Sherwood Sandstone Group formation (at Sellafield)
STZ	Saline Transition Zone
TDS	total dissolved solids
T_h	homogenisation temperature of fluid inclusions
Th	thorium

Tl	thallium
U	uranium
VISUAL-BALAN	computer program for modelling hydrological mass balance
WP	Work Package
wt %	weight of component as percentage of total
XRD	X-ray diffraction
XRF	X-ray fluorescence spectrometry
Y	yttrium
Zr	zirconium
$\delta^{18}O$	$^{18}O/^{16}O$ ratio, expressed as deviation from a standard
$\delta^{13}C$	$^{13}C/^{12}C$ ratio, expressed as deviation from a standard
ΣREE	total REE concentrations
1D	one dimensional
^{2}H	deuterium (hydrogen isotope with atomic mass 2)
2D	two dimensional
3D	three dimensional
^{13}C	carbon-13 stable isotope
$^{13}C/^{12}C$	isotopic ratio of carbon-13 to carbon-12
^{14}C	carbon-14 isotope, radioactive with half-life 5730 years
^{18}O	oxygen-18 stable isotope
$^{18}O/^{16}O$	isotopic ratio of oxygen-18 to oxygen-16
$^{87}Sr/^{86}Sr$	isotopic ratio of strontium-87 to strontium-86
‰ PDB	per mil deviation of stable $^{13}C/^{12}C$ or $^{18}O/^{16}O$ ratio versus the PDB standard (expressed as $\delta^{13}C$ or $\delta^{18}O$)

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